The Journal
of the
SOCIETY OF DYERS
AND COLOURISTS

CONTENTS

Proceedings of the Society

Symposium on "Bleaching, Dyeing, and Finishing Today"

The Society held its seventh Symposium, on "Bleaching, Dyeing, and Finishing Today", at the Northern Counties Hotel, Portrush, Northern Ireland, on Wednesday–Friday, 14–16th September 1955. The attendance at the technical sessions exceeded 200, including several from the Continent and Scandinavia.

Opening of the Symposium

Wednesday, 14th September 1955, at 10.30 a.m.

The Symposium was formally opened by the President of the Society (Mr. FRED SMITH)

Mr. SMITH said that Portrush was an ideal setting for the Symposium. The Symposium Committee, under the chairmanship of Mr. D. A. Derrett-Smith in Northern Ireland and Mr. N. Hamer in England, had arranged for the presentation of thirteen papers, all of which would be of great value for the processing of Ulster's fine-quality linen and the man-made fibres which were beginning to compete with it. In all papers there was substance for the practical and the technical, and ideas for future research by the purely scientific.

The Symposium Dinner

The Society's Symposium Dinner and Dance was held on Thursday, 15th September 1955, under the presidency of Mr. Fred Smith.

"THE SOCIETY OF DYERS AND COLOURISTS"

After the toast of "Her Majesty the Queen", that of "The Society of Dyers and Colourists" was proposed by—

The Right Honourable G. B. HANNA, Q.C., M.P. (*Minister of Home Affairs in the Government of Northern Ireland*), who said that he had experienced three emotions when he had been invited to propose this toast: firstly pleasure, since Mr. R. J. G. Reid (Chairman of the Northern Ireland Section) was an old friend of his; secondly embarrassment, as he had no knowledge of the jargon used by dyers and colourists, except that fast colours would not run; and thirdly he was intrigued to know why he had been asked, for he had no colouristic qualifications. His maternal grandfather had been a bleacher, and his paternal ancestors had been concerned with dyeing and finishing. His father, as a younger son, had been sent into the profession which would be the most useful to them— the law. He himself, as a barrister, had had to whiten characters, and as a minister he had put the finishing touches.

He had turned for enlightenment, as a good minister should, to the scriptures. In Exodus we are told that the offerings of the children of Israel were to include "blue, and purple, and scarlet, and fine linen, and goat's hair, and ram's skins dyed red"— a further link between Ulster and Israel. In Genesis, Joseph's coat of many colours was an early indication of the dyer's art,

but its sad fate had put such coats out of fashion since then.

In the past, dyeing had been a home industry, carried on by women, but in modern times most women put more colour on their face and hands than on their clothes.

The fifteenth century was of special significance, for in 1472 the Worshipful Company of Dyers of the City of London was granted its charter of incorporation. Twenty years later America was discovered, and thus the 'u' was taken out of "colour".

He had read that there were seven spectral colours, but in Ireland only two— orange and green— were of significance. Perhaps a little yellow might be added for those pusillanimous Irishmen who had no party. Almost any colour could be produced by suitable mixing of the primary colours, but orange and green together frequently resulted in blood— red or blue according to ancestry.

The Society had carried on for over seventy years its grand work of providing meeting places for those interested in the art and science of dyeing. He had thought it interesting to see what matters concerned Parliament in the year in which the Society was founded. According to *Hansard*, on 28th February 1884 questions were asked on the following three topics— the possibility of installing electric lights in the British Museum (No: no funds available from the Government); a mutiny in the Sudan; and the nature, character, and tendencies of the Orange Society. These subjects were still of parliamentary interest today.

Mr. Hanna paid a tribute to the enthusiasm of the young Northern Ireland Section, and extended a warm welcome, on behalf of both the government and the people of Northern Ireland, to the Society. He wished the Society a successful, happy, and worthwhile symposium. One of the meanings of "symposium" was a drinking party, but he wondered whether a "shrinking" party would be more appropriate. He wished them a merry feast— "eat, drink, and be merry; for tomorrow we dye".

Mr. FRED SMITH (*President of the Society*) expressed the Society's deep sense of honour at having the Minister as chief guest at the dinner, and thanked Mr. Hanna for his witty and entertaining speech. He had asked Mr. R. J. G. Reid to make the formal response to the toast, in view of Mr. Reid's great work for the Northern Ireland Section and for the Society.

Mr. R. J. G. REID (*Chairman of the Northern Ireland Section*), on behalf of the President and the members of the Society, thanked Mr. Hanna for proposing the toast of the Society in such humorous, generous, and complimentary terms. Mr. Hanna, in his high office as Minister of State for Home Affairs, knew something of the importance people attach to colour. In Northern Ireland they liked a little flagwaving, and if the right colour were not used the Minister had a good method of damping enthusiasm.

Mr. Hanna had spent his early years in Ballymena, where his father had been a distinguished lawyer, and his great uncle had owned a dyeworks at Kildrum, so that he had been born into a dyeing community. Ballymena was in the midst of an extensive dyeing region, and they in Northern Ireland knew the importance to bleaching and dyeing of the Maine, Braidwater, Kellswater, and Six-mile rivers, to which could be added the Bann, Lagan, Rhone, Claudy, and others. Bleachers and dyers become quite attached to rivers, which they often refer to as "water", and in the works on the banks of these "waters" millions of yards of linen, cotton, wool, and rayon have been bleached and dyed over the years, and then exported to all parts of the world—something of which we are justly proud. Some maintain, perhaps rightly so, that these "waters" have an important bearing on the high quality of the "Irish finish".

It is the managing directors, managers, chemists, dyers, and bleachers from these works who form a high percentage of the local Section, which proudly boasts a membership of 130, including some eight members from Eire. whom we are delighted to have. The Section was inaugurated when Dr. C. M. Whittaker was President of the Society, and we are much indebted to him, to Dr. H. A. Thomas, and to other members of Council for their wise guidance at that time; and we are grateful for the encouragement received, not the least from our esteemed President, Mr. Fred Smith. During our nine years we have had over sixty technical lectures, some held in conjunction with our good friends of the Textile Institute. These lectures have provided us with valuable information on the application of dyes, which in turn has reflected favourably on the quality of our dyeing— something of high practical value.

We feel highly honoured and greatly encouraged that the Council decided to hold this Symposium in Portrush, and as Chairman of the Northern Ireland Section may I extend to you all a hearty welcome! This is a great day for the Irish. The high-level lectures presented to us contain plenty of food for thought, and we are much indebted to the authors. Outside the lecture room we have ample opportunities for social activities and for meeting old and making new friends: all work and no play would make dyers dull boys.

I should like to mention how grateful we are to Mr. Frizzell, Secretary of the Northern Ireland Tourist Development Association, for his good service in assisting us with transport and hotel arrangements.

H. G. Wells said about writing: "Once a writer, always a writer. You start about three years old and leave behind an unfinished manuscript." So we can say of dyers: "Once a dyer, always a dyer; and we hand over our task to a new generation with many problems unsolved."

The Society is a progressive organisation and has much new work to do, although in the seventy-one years of its existence it has made a tremendous contribution, both scientific and technical, in the field of colour, which has been recognised internationally by other scientific organisations. This international recognition is a great tribute to the Society and reflects much credit on the far-sighted founders and on those who, over the years, have given many hours of their valuable time to extending the work of the Society.

In this rapidly changing scientific age those who administer the affairs of the Society and those who serve on the technical committees are confronted with the problem of keeping abreast of the times. This has been clearly borne out by the complexity of the problems dealt with in the Symposium papers.

I would like the ladies to know that the majority of coloured goods they purchase today have been tested for fastness by methods established by the Society, and many of these test methods have been accepted by the International Standards Organisation. The standards, of course, vary according to the material and the dyes used. Where washing instructions are given with a garment, it is important that these are adhered to.

A most important event in the life of the Society takes place next year, when the centenary of the discovery by William Henry Perkin of the first synthetic dye obtained from coal-tar will be celebrated in London. The Society has been foremost in promoting this important celebration in conjunction with other leading scientific organisations. There is no more coveted distinction in the field of dyeing than the Perkin Medal presented by the Society.

"THE URBAN DISTRICT COUNCIL OF PORTRUSH"

Mr. D. A. DERRETT-SMITH (*Chairman of the Symposium Committee*) said that it was one

Saturday in November 1954, in that same hotel, that the Symposium Committee first had the pleasure of meeting Mr. W. R. Knox and his colleagues of the Portrush Urban District Council. He had explained to Mr. Knox that in the Society we refer to a gathering of this kind as a "symposium" rather than a "conference", and he had given Mr. Knox the familiar classical definition of a "symposium"— it was originally a drinking feast, usually with dancing girls in attendance. The gales of laughter had shown that Mr. Knox possessed that priceless gift— a sense of humour.

The Society's symposia differ somewhat from the original kind. We meet on these occasions to discuss such serious technical matters as the dyeing, bleaching, and finishing not only of the natural fibres but also of the newer synthetic fibres. However, we do not devote all our time to these serious matters, but do try in our less serious moments to arrange that the thirst can be quenched in moderation and that those who set out on the ballroom floor should have at least a reasonable choice of partners.

Mr. Knox had at once agreed to recommend a substantial grant from his Council towards the cost of producing the brochure for the Symposium, and to lend us the colour blocks for the attractive picture on the front cover. This help was deeply appreciated by the Society.

Further, Mr. Knox had introduced the Committee to Captain Williams, Secretary of the Royal Portrush Golf Club, who had very generously offered us the use of the various courses and the amenities of their very attractive clubhouse. We were very pleased to have present at the Dinner Mr. Bob Hanna, an esteemed member of the Section and this year's Captain of the Club.

Our best thanks were due also to Captain Shutt, Entertainments and Sports Officer of Portrush, for arranging that the many sports facilities of Portrush were made available to those attending the Symposium.

In drinking the health of Mr. Knox and his colleagues of the Urban District Council of Portrush we would be expressing our gratitude for all that they had done for us.

Mr. W. R. KNOX (*Chairman of the Urban District Council of Portrush*) cordially welcomed the Society to Portrush. Since their only industry was the tourist industry, they were concerned to encourage the holding of as many conferences and symposia as possible at Portrush. He was very pleased to learn that the attendance was beyond anticipation, especially in view of the long distances travelled by most of those present.

In very early times Portrush had been the scene of wars between various Ulster tribes, and at one time mariners were lured on to the rocks. Its great development as a holiday centre had taken place during the past 50–70 years. The famous golf courses at Portrush, its catering facilities, and the nearness of such tourist attractions as the Giant's Causeway enabled it to merit the title of the "St. Andrews of Ireland".

Mr. Knox wished those present a safe return home and good fortune in the future. He hoped that the Society would return to Portrush after not too long an interval.

PRESENTATION OF THE SOCIETY'S SILVER MEDAL TO MR. J. PORTER

Mr. FRED SMITH (*President of the Society*), in presenting the Silver Medal to Mr. J. Porter, said that the success of the Symposium was a tribute to the work of Mr. Porter and the Northern Ireland Section Committee. The Council deeply appreciated the value of over eight years' really hard work put in by Mr. Porter, and the medal was a reward for truly voluntary service.

JAMES PORTER

Silver Medal for outstanding services to the Society, notably in the inauguration and the development of the Northern Ireland Section

Mr. JAMES PORTER (*Honorary Secretary of the Northern Ireland Section*) expressed his gratitude for the award, and said that he regarded it as a compliment to the Northern Ireland Section as a whole. He was very pleased that all former and present Chairmen and Committee Members were present that evening, and he thanked them for all their help, and also the staff at the Society's offices in Bradford.

Some Aspects of Present-day Bleaching Practice

N. F. CROWDER and W. A. S. WHITE

A general review is given of present-day practice for bleaching the principal textile fibres, the emphasis being mainly on cotton. Modern trends and developments are discussed, including methods of continuous bleaching and the use of sodium chlorite. Experimental results are quoted in connection with the peroxide bleaching of cotton at various pH values and the application of peroxides for combined desizing, scouring, and bleaching of rayon-staple fabrics.

Introduction

The aim in this paper is to give an indication of the present "state of the art" and the trend of developments in the bleaching of various textiles. Undoubtedly, bleaching still occupies an important place in textile processing. The natural fibres, with their various impurities and rather drab natural colours, are still predominant, and have to be bleached to give a pure white finish and often to prepare them for dyeing and printing. The need for bleaching has diminished to a certain extent with the great increase in the use of rayon, particularly as an alternative to cotton. A further diminution may be expected as a result of the increasing use of synthetic fibres made from colourless polymers, but so far their impact on textile bleaching has been comparatively slight. On the other hand, the technique of bleaching is becoming more and more complicated as the number of fibres increases and as the use of blends becomes more common. Also, the bleaching process has to keep pace with the continual urge for greater productivity as well as with the demand for improved standards arising from the introduction of new dyeing techniques and the increasing discrimination of textile buyers.

Cotton

It is estimated that, of the cotton spun in this country, approx. 20% is used for industrial purposes where bleaching is not normally required. The remainder is divided in approximately equal proportions between apparel and household uses, a considerable proportion of the cotton used in these categories being bleached either for white finish or as a prepare for dyeing or printing.

In practice a wide variety of bleaching techniques are employed, because of considerable variation in the standards required in respect of colour and absorbency. Further, the severity of the scouring and bleaching treatments required to produce a given result depends on many factors, including—

(1) The type and the colour of the original cotton

(2) The cleanliness of the material, particularly in respect of motes

(3) The twist and the count of the yarn

(4) The construction of the fabric.

The aim of the bleacher should be to remove the non-cellulosic impurities to a sufficient extent for the purpose for which the material is intended without affecting the cellulose to any significant extent. The impurities which present the greatest difficulties are undoubtedly the natural wax, seed fragments, and oil stains.

The main bleaching agents used in commercial practice are—

(1) Sodium hypochlorite

(2) Calcium hypochlorite (prepared from bleaching powder or from liquid chlorine and slaked lime suspension)

(3) Hydrogen peroxide

(4) Sodium peroxide

(5) Sodium chlorite.

In addition, alkalis, detergents, mineral acids, and desizing agents are employed at various stages.

PIECE GOODS

Cotton piece goods are generally scoured and bleached in rope form because it is invariably cheaper to operate in this way, but certain types of cloth require to be treated at open width. The type of plant depends also upon the particular bleaching process employed and upon the scale of operations. The latter is a most interesting aspect, because in this country the largest bleachworks almost always operate on a commission basis and a variety of fabrics are handled, many of which have to be bleached to different standards. The problems facing the British bleacher are, therefore, very different from those in the United States, where bleachcrofts are often an integral part of a vertical organisation and long runs of similar types of fabric can be arranged. This is probably the main reason why the continuous bleaching methods now in operation in America have not been widely adopted in this country.

Desizing is a useful preliminary to all kinds of scouring treatments, particularly where for one reason or another the cloth is not given a very thorough alkali scour. The old-fashioned rot steep is still used to a certain extent, as also is the acid

steep or "grey sour". Treatment with malt or other enzyme preparations under appropriate conditions is the most effective method of removing starch sizes, and is being increasingly employed. An efficient desizing treatment should be regarded as a necessity in the case of goods containing vat-dyed threads, which might otherwise bleed during the alkali scour in the presence of starch degradation products.

The alkali scour is undoubtedly one of the most important stages in cotton bleaching, and many of the difficulties which arise in dyeing or printing can be traced back to inadequate or irregular scouring. Kier boiling under pressure gives by far the best results, particularly when hypochlorites are used for the actual bleaching. A review of the developments in plant for alkali boiling is given by Hvattum and Turner[1]. The pressure kier boil is essentially a batch process, and the only development to shorten this stage which is in use at present, apart from the use of auxiliaries in the scouring liquor, is the Mather waggon kier, with which the actual loading and unloading can be performed outside the kier. Many methods have been suggested for streamlining the process and making it continuous before and after the kier boil stage, Gantt pilers and J boxes being used for the operations of desizing, souring, and hypochlorite treatment.

Several types of woven fabrics such as heavy drills develop permanent creases or friction marks if processed in rope form, and it is then essential to operate at open width. At the other end of the scale medical gauzes, which are too fragile to treat in rope form, are also processed at open width, several layers of cloth being treated together. Open-width scouring under pressure can be carried out in special kiers of the Jackson or Smith type, which are essentially jigs operating under pressure.

Fabrics containing coloured threads usually cannot be given a pressure boil, and the lack of a thorough scour can be overcome by giving a double hypochlorite treatment, with intermediate sour and soda ash boil when necessary. Alternatively, peroxide can be used in place of hypochlorite, or if a high colour is required after the first hypochlorite stage.

Fabrics made from highly twisted yarn usually require a very thorough scour to remove sufficient wax to obtain good absorbency. Even light-weight fabrics such as typewriter cloth may require two or even three kier boils under pressure to produce good absorbency, whereas much heavier cloth composed of soft-spun yarn may respond to less vigorous treatments. It is of interest to note that in practice cloth which is comparatively easy to scour is often given two kier boils with an intermediate rinsing and repacking to ensure level results.

Hypochlorite Bleaching

Hypochlorite treatment of woven piece goods is usually carried out by piling the material into glazed brick or tile-lined tanks and circulating the chemic liquor through the pile. The best practice is to turn the load into a second tank, so that the end which entered first is also drawn out first. An alternative system of chemicking is to impregnate the cloth with hypochlorite in a washing machine and then stack it for several hours while bleaching takes place. By using a Gantt piler the treatment can thus be made continuous, and this procedure is employed by some printers. Saturation and piling tends to give rather higher fluidities than chemicking in tanks, and the latter procedure is generally employed when bleaching to full white.

The rate of bleaching and the rate of degradation of cellulose increase with the temperature, and to avoid variations a lower concentration of hypochlorite is commonly employed in summer, because it is not usually convenient to vary the time of treatment. Alternatively, a standard temperature of, say, 70°F. may be employed throughout the year.

The concentration of hypochlorite bleaching liquors for cotton is usually between 1 g. and 3 g. available chlorine per litre, and is best estimated by means of the standard thiosulphate or arsenite titration rather than by measuring the density with hydrometers. The density of the bleaching solution, depending as it does upon the total solids in solution, can be particularly misleading when chemic liquors are repeatedly refreshed.

Most commercial hypochlorite bleaching is carried out at pH values between 9·5 and 11·0, because it has been shown that the rate of degradation of the cellulose increases unduly as the pH of the liquor approaches the neutral point[2,3]. The bleaching reaction is always accompanied by a tendency for the pH value to fall, and hence careful control of the pH is necessary, particularly when chemic liquors are retained and refreshed for succeeding batches of cotton. Narrow-range indicator papers, pH 8·5–10·0, provide a useful means of checking the pH in works practice, the readings thus obtained being in good agreement with pH determinations made with a glass electrode.

Sodium hypochlorite has replaced bleaching powder to a large extent in areas where it is practicable and economic to obtain delivery of concentrated sodium hypochlorite liquor containing 14–15% available chlorine. When the sodium hypochlorite consumption is large enough to justify bulk delivery, the effective cost is substantially the same as when using bleaching powder. Sodium hypochlorite has the practical advantages of being ready for immediate use and not requiring any dissolving arrangements; also there are no sludge disposal problem and no danger of specks of lime being deposited on the cloth. It has an important advantage over calcium hypochlorite chemic in that there is a much greater reserve of soluble alkali, and consequently less tendency for the pH value to fall during bleaching. If desired, extra alkalinity is easily obtainable by addition of soda ash. The use of sodium hypochlorite reduces the amount of acid required for souring, and frequently enables sulphuric acid to be used in place of the more costly hydrochloric acid.

Peroxide Bleaching

The advent of hydrogen peroxide and sodium peroxide in commercial quantities provided an alternative to the hypochlorites for bleaching cotton. A review of the literature on peroxide bleaching and its relation to other bleaching methods was undertaken by the AATCC in 1950[4].

One of the principal differences between hypochlorite and peroxide bleaching is that the latter is capable of continuing the scouring action simultaneously with the bleaching action. Satisfactory results can, therefore, be attained after milder scours, and in some instances it is possible to use a single-stage combined scour and bleach. Another important difference is that with hypochlorite it is essential to remove all traces of residual bleaching agent and the chloramines which it may form in combination with nitrogenous matter. Thorough rinsing followed by souring or anti-chlor treatment is, therefore, required, whereas with peroxide a comparatively short rinsing suffices. It is found that after mild scouring treatment a more permanent white and rather better absorbency are given by bleaching with peroxide than with hypochlorite. Also, peroxide bleaching is in general less liable to have an adverse effect on dyed threads.

At one time it was thought that a peroxide bleach in kiers would enable the normal kier boil with alkali to be eliminated in the case of cotton piece goods. In practice, however, the alkali boil is required for a full white. In theory it should be possible to scour, wash, and peroxide-bleach in the same kier without removing the goods, but in practice it is found advisable to turn the load into a second kier for the bleaching stage and to give intermediate rinsing in machines. Solutions of the order of 0·3–0·7 volume strength, stabilised with sodium silicate, are employed in presence of a small proportion of caustic soda or soda ash. In general, the stability of the bath varies inversely with the amount of alkali present and with the temperature; conditions are, therefore, adjusted so that uniform bleaching is obtained in a reasonably short time. Thus at pH 10·5 a kier load can be satisfactorily bleached in 5 hr. at 180°F. or overnight at 150°F.

When hydrogen peroxide is employed, the necessary amount of caustic soda or soda ash is added along with the silicate when preparing the bath. With sodium peroxide the procedure is slightly different, because this product yields both hydrogen peroxide and caustic soda when dissolved in water. The amount of caustic soda thus formed is usually more than is required, and to obtain the required alkalinity a certain proportion of the caustic soda is neutralised by an addition of sulphuric acid. If only carbonate alkalinity is required, the remaining free caustic soda is converted to sodium carbonate by making an appropriate addition of sodium bicarbonate[5].

The degrading effect of peroxide bleaching solutions on cellulose is less influenced by variations in pH value, concentration, and temperature than is the case with hypochlorite. This fact, together with the more innocuous nature of the decomposition products, makes peroxide bleaching rather safer. On the other hand, the degrading effect of peroxides is greatly accelerated by traces of metallic compounds, notably copper and iron when these are in contact with both the cloth and the bleaching solution. The pH value of the peroxide solution is also important, particularly if the fabric has been well scoured beforehand. Thus a peroxide bath of high pH value may be advantageous when bleaching raw or partly purified cotton, but may cause degradation of the cellulose if the cotton has been previously subjected to a thorough kier boil or partly bleached. We have studied this point, and conclude that it is advisable to keep the pH value below 11 in such circumstances, preferably around 10·5. When kier-boiled cloth is peroxide-bleached at pH 10·5, low fluidities can be obtained whether the alkalinity of the bath is derived from caustic soda or soda ash, or whether the bleaching agent is sodium peroxide or hydrogen peroxide. Experimental evidence in support of these points is given in the ensuing sections.

Effect of pH on the Degradation of Cellulose

A plain-woven grey cotton cloth weighing 7 oz./sq.yd. was subjected to three different preparatory treatments, and then peroxide-bleached at pH 11 and pH 10·6 respectively. Details of these preparatory treatments are as follows—

OPEN SCOUR—Treated at the boil for 3 hr. with caustic soda solution (10 g./litre)

KIER BOIL—The material was treated on the commercial scale by a process involving desize → double kier-boil → sour.

CHLORITE BLEACH—Scoured at the boil for 3 hr. with caustic soda (10 g./litre) and then treated with sodium chlorite solution (2 g./litre) at pH 4 for 3 hr. at 195°F.

The subsequent peroxide treatment was for 4 hr. at a liquor ratio of 5 : 1, the temperature being 140°F. for the first 2 hr. and 175°F. thereafter. The two baths employed were as follows—

		Bath A	Bath B	
Peroxide concentration	...	0·8	0·8	vol.
Sodium silicate (J 81)	...	7·0	7·0	g./litre
Caustic soda	...	1·2	—	g./litre
Soda ash	... ...	—	3·0	g./litre

TABLE I

Bath	pH Value Initial	pH Value Final	Oxygen Content (vol.) Initial	Oxygen Content (vol.) Final	Fluidity Before H₂O₂	Fluidity After H₂O₂
			OPEN SCOUR			
A	11·1	11·1	0·78	0·18	2·2	3·9
B	10·4	10·3	0·78	0·41	2·2	3·1
			KIER-BOILED			
A	11·1	11·1	0·78	0·21	2·5	9·5
B	10·4	10·4	0·78	0·17	2·5	6·8
			CHLORITE-BLEACHED			
A	11·1	10·9	0·78	0·37	2·9	7·9
B	10·4	10·3	0·78	0·35	2·9	6·1

The results of the experiments are shown in Table I. It is obviously desirable that the pH value of the peroxide bath should be kept below 11 when treating cotton which has been previously subjected to thorough purification or part bleaching.

Comparison of Sodium Peroxide and Hydrogen Peroxide

In this experiment a cotton sheeting which had been given a commercial kier boil with caustic soda was bleached with sodium peroxide and hydrogen peroxide solutions respectively, both at pH 10·5 and a peroxide concentration of 0·75 vol. Bleaching was for 7 hr. at 150°F. with a liquor ratio of 5 : 1, and in all cases the peroxide solutions contained 7 g. of sodium silicate per litre. The baths were as follows—

BATH 1— Hydrogen peroxide with 0·5 g. caustic soda per litre

BATH 2— Hydrogen peroxide with 3 g. sodium carbonate per litre

BATH 3— Sodium peroxide, alkalinity adjusted to 0·5 g. of caustic soda per litre by addition of sulphuric acid

BATH 4— Sodium peroxide, alkalinity adjusted to 3 g. of sodium carbonate per litre by addition of sulphuric acid and then sodium bicarbonate.

TABLE II

Bath	Average pH Value during Peroxide Bleach	Fluidity after Bleaching	Whiteness (% reflectance at 4700 A.)
1	10·5	3·8	88
2	10·4	4·1	88
3	10·5	4·3	88
4	10·4	4·5	88

From the results given in Table II it is evident that at pH 10·4–10·5 low fluidities are obtainable with either hydrogen peroxide or sodium peroxide, and it is immaterial whether the alkali present is caustic soda or sodium carbonate. When using sodium peroxide, Bath No. 4 is in practice preferable to No. 3, because the pH value is less influenced by any errors in the weighing of the neutralising agents. This latter consideration is applicable mainly in the case of kier-boiled or part-bleached cotton, where the pH of the peroxide bleach has to be more carefully controlled. With grey or partly scoured cotton, where the pH may be higher, the partial neutralisation of sodium peroxide can be readily effected with sulphuric acid alone.

Hypochlorite-Peroxide Processes

Processes involving the use of both hypochlorite and peroxide are generally considered too expensive, not so much because of the extra cost of the chemicals but on account of the extra handling costs. Nevertheless, their use is tending to increase, and they have particular advantage in cases where thorough kier boiling is not given, e.g. cotton–rayon mixtures and colour-woven goods. Mild conditions can be employed in the hypochlorite stage, and the bleaching completed safely in the peroxide bath, which latter acts also as an anti-chlor. The use of peroxide after hypo-

chlorite is not new, and is one of the variations suggested in the Mohr process[6], which is still employed on the Continent. In this process there is a special kier which can be evacuated and also pressurised to ensure thorough penetration of the liquors into the load, so that the scour, hypochlorite, and peroxide stages can be carried out in the same vessel. In the Ce–Es process[7] the goods are impregnated in cold alkaline hypochlorite solution and then transferred to peroxide without rinsing.

Sodium Chlorite

Although sodium chlorite is not widely employed, it has important technical merits for bleaching cotton. Under practical conditions there is little or no tendency to degrade the cellulose, and in addition chlorite will give a permanent white coupled with excellent mote removal on cotton which has not been kier-boiled. Souring and anti-chlor treatments are not required and, if desired, the bleaching can be carried out in a continuous manner employing pad–steam techniques. The most effective bleaching of cotton is obtained at a pH of approx. 4·0 and a temperature of 190–195°F., the concentration of chlorite being approx. 2 g./litre. Less chlorite is required if the material has been previously scoured with alkali, and the alkali scour may be desirable in order to give good absorbency. Very high whites are given by the sequence chlorite → peroxide. The rate of bleaching falls rapidly with increasing pH, as shown in Table III, which gives the minimum times required to bleach a desized Indian cotton pillow fabric to a definite standard of whiteness with chlorite solution (2 g./litre) at various pH values. The temperature was 195°F. throughout and the liquor ratio 20 : 1.

TABLE III

pH Value	Bleaching Time (hr.)
4	2½
5	6
6	19
7	36

At pH values below 4 bleaching tends to be irregular and there is excessive evolution of chlorine dioxide fumes. Even at pH 4–5 a certain amount of chlorine dioxide is evolved, and the bleaching solution is extremely corrosive to metals, including stainless steel. The corrosion difficulty may be partly circumvented by pad application of a cold chlorite solution followed by steaming[8], and this system also has the advantage of requiring rather less chlorite than an immersion bleach.

Many attempts have been made to overcome the corrosion and fume problems. Thus, it has been stated that a mixture of chlorite and hypochlorite at pH 8·5–10·0 is non-degrading to cellulose[9], but it is doubtful whether much advantage is shown over hypochlorite alone[10]. The suppression of chlorine dioxide by the addition of hydrogen peroxide has been suggested[11], but, although this is effective at pH 4·0–7·0, there is some deterioration in bleaching efficiency. Activation with

persulphates above pH 7[12], aldehydes at pH 3–7[13], bromides[14], salts of cobalt, nickel, and manganese at pH 5–8·5[15], sulphur, selenium, or finely divided carbon[16], and chlorinated hydrocarbons[17] have been proposed, and also activation by organic esters such as ethyl lactate (1–3 g./litre) with the addition of sodium nitrate (1–3 g./litre) to inhibit corrosion[18].

The corrosion of plant by dilute acidified solutions of chlorite has been studied by Meybeck[19], who found that polyvinyl chloride and polythene are resistant, but unsuitable, as they are thermoplastic. Cathodic polarisation can be employed to a limited extent to inhibit corrosion of stainless steel, although the best method is to use special equipment lined with chemically resistant tiles set in a suitable cement, usually of the rubber latex type.

We have found that chlorite-bleached cotton does not show the phenomenon of "aniline pinking", which takes place when cotton which has been bleached with hypochlorite is exposed to an atmosphere containing traces of aniline or allied amines. A chlorite bleach should, therefore, be a satisfactory alternative to the normal peroxide bleach on cotton goods for use in the rubber trade.

Continuous Bleaching

Spectacular developments have taken place during the past few years in the continuous processing of cotton piece goods, particularly in the United States. This trend will, no doubt, continue in view of the pressing need to increase, not only the volume of production, but also the production per man-hour under present-day conditions.

From certain points of view a continuous process is simpler to develop from laboratory experiments to large-scale production than is the case with batch methods. The conditions of continuous processing are such that only comparatively small amounts of cloth are being treated at any given moment, whereas when large batches of cloth are being treated, as for example in kier boiling, it is almost impossible to simulate the true practical conditions on a small scale. Nevertheless, the textile engineering problems in developing continuous processes were of considerable magnitude. It has been stated[20] that in 1952 over 65% of the total bleaching of cotton piece goods in the United States was performed by continuous methods, which represents a greater yardage than all the bleaching carried out in this country. The three main processes which have been developed in the U.S.A. are as follows—

(1) DU PONT PROCESS—This process consists of two basic steps. The fabric is first padded in a 2·5–4·0% caustic soda solution, squeezed so that it contains its own weight of liquor, and passed through steam in a tubular preheater[22]; then the hot fabric is retained in an insulated J box for about 1 hr., after which it is rinsed in suitable continuous washing machines. The cloth is then padded in a 0·5–1-vol. peroxide solution at pH

10·5–10·8 in the presence of sodium silicate, preheated to 195–210°F. by steam or a mixture of steam and air, and retained in a second J box while bleaching takes place, after which the goods are again washed continuously. The effects of concentration of caustic soda and peroxide and of times and temperatures of treatment have been given by Campbell[21], and the characteristics of cotton fabrics processed by this system have been described by Bell and Stalter[23]. The goods can be singed and desized before treatment. Souring before the first stage results in the bleached cloth having a lower wax content, while souring between the stages or particularly after the peroxide treatment produces fabrics having a low ash content[21]. Mercerising can be carried out before or after the process, and it is interesting to note that the process was first put forward as a method for bleaching grey mercerised cotton[24]. The ratio of caustic soda to silicate has to be controlled, and a rapid method of estimation based on sodium fluoride has been developed for works use[25]. Speeds of the order of 150 yd./min. are used in practice, and a production of 1·0–1·5 million yards per week per plant is possible.

(2) BECCO PROCESS—This process[26] was developed by the Buffalo Electro-Chemical Co. Inc. Frequently the goods are first given a grey sour by saturating in a 0·2% solution of hydrochloric or sulphuric acid, squeezing, and holding for a few minutes in a scray or small J box. This is followed by washing and padding in 3–4% caustic soda solution. The goods are then squeezed and piled direct into a specially designed J box, where they are heated in steam and held for about 1 hr. It is claimed that temperatures as high as 217°F. are attained under these conditions. Phosphates, silicates, or synthetic detergents are sometimes added to the caustic soda to facilitate scouring, and the addition of small amounts of peroxide is practised when coloured goods are being processed so as to avoid reduction of the dyes. After being rinsed, the goods are padded in peroxide solution containing sodium silicate and caustic soda; synthetic detergents are also added in some instances. After steaming in a second J box, the goods are washed in either tight or slack rope washers. The former give the faster output, but the latter are usually more efficient per unit of water used. The saturators and J boxes can be designed to run at any speed, and the upper limit is set by the washing machines. During the past few years several new types of washing machines have been designed to run at high speeds.

The essential difference between the du Pont and Becco systems is that in the former the cloth is preheated before being retained in the J box, while in the latter the heating is carried out during the storage. Both processes can be operated at open width, although lower speeds have to be used. The cloth is lapped into the J boxes and withdrawn through a slot, but it is not easy to avoid crease marks on susceptible fabrics owing to the weight of fabric which has to be held in the J box at any given time. The du Pont system has been adapted

for processing knitted fabrics by a single-stage scour and bleach using one J box, and the fabric can be run at speeds up to 150 yd./min.[27]

(3) MATHIESON PROCESS— This process[28] is primarily intended for operation at open width with the minimum of tension on the fabric. The cloth is scoured by padding in a hot (180°F.) solution of caustic soda (4–8%) containing a wetting agent to ensure thorough penetration, and is then drawn into a steamer, where it is plaited on to a slowly moving conveyor by the action of steam jets. It is withdrawn from the conveyor at the exit end of the steamer, and washed in an open soaping range without allowing any intermediate cooling. The time of steaming can be varied from 30 to 60 min. by altering the speed of the conveyor. The bleaching stage can be carried out with peroxide using similar apparatus, or by means of acidified sodium chlorite. Speeds of 60–100 yd./min. are claimed.

A variety of cloths can be treated by the American processes by adjusting the conditions to suit the particular fabric, but for economical working it is very desirable to have long runs of one type of fabric.

Smaller-scale plants such as the Butterworth Junior continuous bleaching unit have been designed in the U.S.A. to handle shorter runs of fabric at lower speeds, and in England Sir James Farmer Norton & Co. Ltd. have produced the Compact continuous bleaching machine, which consists of two tensionless-rope washing machines, an impregnator, and a small J box having a capacity of up to 1000 lb./hr. Two of these units can be used in series for scouring and bleaching.

The alkaline pad–steaming sequence has been examined by Hvattum and Turner[29] with particular reference to the loss in weight and residual wax content of yarn. It has been shown on yarn that cotton which would meet many technical requirements with regard to absorbency and freedom from impurities can be produced by short times of steaming after padding in caustic soda solution of 8–10% concentration containing a wetting agent.

In Europe the problem of the continuous bleaching of cotton piece goods has been approached from other directions, including the following—

DEGUSSA* PROCESS— This process[30] is based on the use of sodium chlorite in porcelain or tile-lined equipment. It is claimed that the entire treatment required to produce a satisfactory result consists in passing wet cloth into an impregnation tank containing sodium chlorite bleaching lye, squeezing, and retaining in a heated J box for 60–90 min. at 200–205°F. The goods are then given an alkaline wash and a water wash. A good degree of bleaching and mote removal is claimed when running at speeds of 30–150 yd./min.

JAGRI† SYSTEM— This comparatively small plant[20] is designed for the continuous bleaching of cloth at open width and appears to be a modern

version of the time wheel. The goods are entered in full width and folded round the drum of the machine, which rotates continuously.

BENTELER SYSTEM— This is a plant[31] for desizing or bleaching at open width in which the fabric can be impregnated, steamed, then held for 30–60 min. in a chamber, where it is batched on and off two rollers on a continuous basis, and washed in specially designed washing machines. The whole plant is enclosed, so that the fabric is not exposed to the atmosphere, and speeds of 45–90 yd./min. are claimed.

Other continuous scouring and bleaching machines intended to handle smaller quantities of material include the Dungler machine[32] for treating cloth at open width, in which steam impinges on the fabric from both sides simultaneously after padding in the scouring or bleaching solution; and the Ganeval and St. Genis machine[33], where the fabric is run on to a horizontal stainless-steel conveyor, which carries it slowly and continuously through the bleaching solution.

Continuous processes based on hypochlorite have also been put forward, but these do not appear to have been adopted on a large scale, possibly because hypochlorite bleaching is not as satisfactory as peroxide after a continuous alkali scour. The Diamond Alkali Co.[34] suggest a three-stage process consisting of hypochlorite, caustic pad–steam, and hypochlorite; while in the method given by the Allied Chemical & Dye Corpn.[35] the goods are scoured by the caustic pad–steam technique, which is followed by multistage bleaching in cold hypochlorite for short periods.

In Britain the conventional process has remained in favour because on the whole it gives a higher standard of bleaching and is more easily adapted to the processing of a wide variety of cloths in comparatively small quantities. The retention of the kier boiling stage is also advantageous at the present time in view of the predominance of cotton containing impurities such as seed husk and motes, which do not appear to be readily removed by the continuous processes so far proposed. As already indicated, the conventional process has been examined with a view to continuous operation on either side of the kier boiling stage. Thus, a semi-continuous process can be employed using Gantt pilers or J boxes in conjunction with horizontal kiers, which is believed to compare favourably with the American continuous processes in respect of production per man-hour.

KNIT GOODS

Cotton knit goods are of necessity bleached in rope form, but it is not practicable to haul this type of fabric from one machine to another, and if it is treated in large batches in a kier great care must be exercised to avoid permanent distortion. Only mild scouring treatments are required because of the open construction, and also it is desirable to retain as much natural wax as possible to give a soft handle. Knit goods are, therefore, commonly scoured and bleached in comparatively small batches in winch machines. Goods composed of American or Peruvian cotton are scoured with

* Deutsche Gold- und Silber-scheide Anstalt.
† Maschinenbau und Apparatebau Jagri.

soda ash and a detergent, bleached with sodium hypochlorite at 90–110°F., and then given an anti-chlor treatment, the whole process taking 3–4 hr. Alternatively, a single-stage combined scour and bleach can be operated using a peroxide solution containing a mild alkali, a detergent, and sodium silicate as stabiliser. For this purpose either hydrogen peroxide and an alkali or a partly neutralised solution of sodium peroxide can be used. Caustic alkalinity is to be avoided, as it may make the goods rather harsh. Hence, when using sodium peroxide, the caustic alkali is almost completely neutralised with sulphuric acid, and the remainder converted to sodium carbonate by addition of sodium bicarbonate as already described in connection with the peroxide bleaching of kier-boiled piece goods. The combined scour and peroxide bleach is usually a slightly quicker process, and there is an obvious saving in the amount of rinsing required. Also the peroxide method tends to give lower fluidities.

For very high whites or with dark-coloured types of cotton more vigorous bleaching is required, and the following alternative processes are in use—

(1) Scour, hypochlorite, sour, scour, hypochlorite, anti-chlor

(2) Oxidising scour with peroxide, peroxide bleach

(3) Scour, hypochlorite, peroxide.

Cotton hosiery made from dark-coloured mercerised yarn can be rapidly bleached by hypochlorite followed by peroxide without a preliminary scour. This shows a considerable saving in time compared with the more conventional method, which is as No. 1 above.

YARN

Although the amount of cotton bleached in the form of yarn is small in comparison with piece bleaching, occasions frequently arise when yarn bleaching is required. Typical examples are preparation for dyeing, bleaching of sewing cotton, and also bleaching of yarn for admixture with wool in the hosiery trade.

At one time cotton yarn was almost exclusively bleached in hanks, which were chained together and processed in the same way as a rope of cloth using pressure kiers, washing machines, and hypochlorite bleaching pits. This method is still in operation, but it is lengthy, and particular care is necessary to avoid unevenness at the points where the hanks are linked together. The modern tendency is to bleach in a more efficient manner in dyeing machines, the yarn being very often in the form of beams, cones, or cheeses, thus eliminating the expensive operation of hank winding. The alkali scour and hypochlorite process is not particularly suitable for yarn in such forms, on account of the difficulty of ensuring satisfactory penetration, and as a result package bleaching is usually carried out by processes involving peroxide. Thus a single-stage peroxide bleach usually suffices as a prepare for dyeing, while for full white a

double peroxide bleach may be required. For dark cotton yarn to be bleached to full white a three-stage process involving oxidising scour → hypochlorite → peroxide gives excellent results. Yarn in hanks may also be bleached in Hussong machines or in pack form. In the bleaching of packages or packed hanks, it is advisable first to wet out the cotton thoroughly.

LOOSE COTTON

Cotton for textiles is very seldom bleached in the loose condition, but large quantities of bleached fibre and linters are required for cotton wool and in the manufacture of cellulose derivatives.

Absorbent cotton for surgical purposes is prepared by thorough pressure-kiering with caustic soda in special kiers fitted with a detachable side-plate or in spherical rotating boilers similar to those employed in the paper trade for caustic digestion of rags, straw, and esparto. Boiling is followed by hypochlorite bleaching, souring with hydrochloric acid to reduce the mineral content, soaping, bluing, and finally rinsing in dilute solutions of citric or tartaric acid to give a "scroopy" handle. Bleaching and souring can be effected in tanks, but washing is best carried out in continuous washing machines similar to the raw-wool scouring ranges.

Linen

The flax fibre contains 25–30% of non-cellulosic matter, mainly hemicellulose and pectins together with lesser amounts of lignin and wax. The bleaching process does not necessarily aim at complete purification, because a substantial proportion of hemicellulose may be retained without detriment. Linen is frequently scoured or bleached in yarn form with a weight loss of approx. 10%, and the bleaching completed after weaving. This is particularly the case with dress materials, suitings, drills, and all fabrics containing dyed threads. Other materials such as cambrics, damasks, and sheetings may be woven from unbleached yarn, in which case all scouring and bleaching is conducted in the piece.

As a general rule, linen is not subjected to such vigorous treatments as cotton, particularly in the scouring stages, but the processes are frequently longer.

YARN

In yarn bleaching the prime objects are to attain a $\frac{1}{2}$ or $\frac{3}{4}$ white with a moderate loss in weight and at the same time to remove "sprit", i.e. woody matter from the stem of the flax plant. At one time the usual process consisted of a number of repetitions of the sequence soda ash scour → alkaline hypochlorite → sour. During the past twenty years, however, the process has been considerably shortened and the amount of cellulose degradation reduced by the use of acidified hypochlorite solutions and peroxides. The basic steps of the modern process are—

Mild scour with soda ash, 8–10% on weight of yarn

Chemic with neutral or acidified hypochlorite solution or with chlorine water, at 3–4 g. available chlorine per litre.

Peroxide steep using sodium peroxide or hydrogen peroxide of approx. 0·5-vol. strength.

Occasionally the sequence soda ash scald → alkaline hypochlorite is used instead of the peroxide stage, but it has no particular advantage and is longer. Sometimes also the sequence alkaline chemic → sour is used at the second stage, but this does not give as good a result as the acid or neutral chemic, which chlorinates the lignins and renders them easily removable in the subsequent alkaline peroxide treatment. Linen yarn is almost exclusively bleached in hank form and presents considerable difficulties in respect of package treatment. Winding must be rather firm to allow for the loss in weight during bleaching, and it is difficult to obtain good penetration of such a package because of the extensive swelling of the fibre when wetted. Further difficulties arise on account of the large amount of colouring matter to be removed and the fact that in package treatment there is little or no tendency for sprit to be mechanically detached. Some coarse dry-spun yarns are, however, successfully scoured and part-bleached in the form of cross-wound cheeses, and as a result a substantial saving is effected in the labour costs of winding and bleaching. Linen hanks are frequently scoured in kiers, chemicked on reels, and then peroxide-treated in pack form in stainless-steel machines. Alternatively, all the operations can be carried out in a Hussong-type machine, but the use of acid chemic is thereby precluded on account of its corrosive nature. When chlorine water is used for chemicking, this is effected in specially constructed tile-lined pots, the chlorine gas being injected into the liquor-circulation system. Chlorine water is attractive on economic grounds and is very effective in removing sprit, but special plant is required and various precautions are necessary to obtain uniform treatment.

CLOTH

Materials woven from ¾ white yarn receive a mild scour and sometimes a desizing treatment followed by a mild alkaline hypochlorite or peroxide bleach.

To obtain the highest and most permanent whites on materials woven from green or boiled yarn it is necessary to scour by the lime → sour → soda ash sequence, which is followed by alkaline hypochlorite and souring. Further turns consisting in soda ash scald → weak hypochlorite → sour are given until the desired result is obtained. Acid chemicking of cloth is advantageous at the first hypochlorite stage, but in practice is less easily carried out than on yarn, which can be reeled out-of-doors. Linen cloth is, however, sometimes acid-chemicked using enclosed winch machines made of wood.

Although cloth-bleaching processes involving the lime boil sequence give the best whites and remove epidermis most effectively, they remove all the hemicellulose and thus lead to a high loss in weight. This is not necessarily a disadvantage, but for some materials it is commercially attractive to produce a reasonably good bleach with only a moderate loss in weight. In weight-conserving treatments the goods receive an ash-caustic steep at temperatures below the boil followed by alkaline chemic and sour. Further "turns" to raise the colour frequently include a peroxide steep at a temperature of 165°F. or less.

SODIUM CHLORITE

Much attention has been devoted to the possible application of sodium chlorite to linen bleaching, and undoubtedly chlorite has important merits for the purpose. It will bleach the natural colouring matter to a marked extent and remove sprit in one operation without significant degradation of the cellulose and without the necessity for a thorough prescouring with alkalis. Chlorite alone does not produce a high white on linen, but the bleaching is very readily completed in a subsequent peroxide treatment. The three-stage process comprising mild scour → chlorite → peroxide will give a good white with low weight loss on all types of linen goods, including cloth woven from green yarns. This is much shorter than conventional cloth-bleaching processes, but the cost of chemicals is high on account of the comparatively high concentration of chlorite required. Special plant must be employed for the chlorite stage in view of the corrosive nature of the bleaching solution. The amount of chlorite may be reduced by part-bleaching with hypochlorite and then using chlorite in the later stages, where its non-degrading action is of particular advantage. A reduction in chlorite consumption may also be effected by carrying out the chlorite treatment in two stages with an intermediate alkali scour[36]. However, these modifications all lengthen the process and so reduce the incentive to install plant suitable for chlorite. Whilst chlorite is used by some linen bleachers on the Continent, it has so far received only limited acceptance in the British Isles.

Jute

The total amount of jute produced is second only to cotton, but a very small proportion requires to be bleached, and then only to a limited extent. Owing to the important part played by the non-cellulosic matter in "cementing" together the very short ultimate fibres in jute, the material suffers a substantial loss in strength if bleached to a pale cream or white. Also, the bleach is not permanent, marked reversion taking place on exposure to light. Where part bleaching is undertaken, it is generally as a prepare for dyeing or printing.

Jute carpet yarn is bleached in hank form with alkaline sodium hypochlorite in Hussong-type machines using 5–7 g. available chlorine per litre. Afterwards the yarn is usually given an anti-chlor with sodium bisulphite, but it is not soured because of the difficulty of removing the last traces of acid. A somewhat improved result is obtained by

prescouring in a neutral detergent such as Lissapol N. A good part bleach for dyeing is also given by treatment in Hussong machines for approx. 1½ hr. at 140°F. with an alkaline peroxide solution—

Sodium silicate	...	5 g./litre
Sodium peroxide	...	3 g./litre
Sodium bicarbonate	...	6·5 g./litre

The chemicals cost is substantially the same as in the hypochlorite bleach, the peroxide bleach having the advantage that, if required, scouring can be effected at the same time by inclusion of a suitable detergent.

For higher colours a hypochlorite bleach at approx. 3 g. available chlorine per litre followed by a peroxide treatment is advantageous, and the degree of bleaching thus obtained is as high as is normally required for jute.

Jute carpet yarn for dyeing can be successfully bleached in the form of cross-wound cheeses by a single-stage peroxide process. Soft-wound cheeses can be bleached in an open machine, but hard cheeses require a pressure machine to obtain a uniform result. A recommended formula is as follows—

		g./litre
Sodium silicate	...	10
Sodium peroxide	...	6
Sulphuric acid (96%)		6
Sodium bicarbonate	...	3
Lissapol N	... ...	1

Treatment is for approx. 45 min. with the temperature rising gradually to 180°F.

Jute piece goods are bleached at open width, e.g. on jigs, using similar methods to those mentioned in connection with the bleaching of yarn in hanks.

Rayon

Filament viscose rayon yarn almost invariably receives a bleaching treatment with sodium hypochlorite during manufacture. After weaving, only a desizing or scouring treatment is normally required. For very good whiteness a bleach with sodium hypochlorite may follow, or alternatively a combined scour and bleach with a 0·25–0·33 vol. peroxide solution containing detergents may be given. Spun rayon is more liable to require bleaching in the piece, because the staple fibre is not bleached during manufacture.

No special difficulties are experienced in bleaching materials composed entirely of rayon, but mixtures of rayon and natural fibres such as cotton require particular care, or otherwise the rayon may be seriously weakened on account of the more thorough treatment required for the other component. With mixtures of grey cotton and rayon it is often advisable to employ the the sequence mild scour → mild hypochlorite → peroxide.

Rayon-staple goods present a particular problem in connection with desizing, because traces of residual starch can impair the handle. Very thorough desizing is necessary, and this is difficult to attain, particularly with heavy or tightly woven goods, on account of the great extent to which the rayon swells in water. Also, there is a tendency for enzyme desizing agents to be partly inactivated by the carboxyl groups in the rayon. The desizing problem is being attacked from two angles—(a) exploration of improved methods of removing starch and its degradation products, and (b) employment of readily soluble sizing materials such as certain cellulose derivatives.

PEROXIDE DESIZING OF STAPLE FABRICS

We have found that under certain conditions highly alkaline peroxide solutions will rapidly remove starch sizes and at the same time achieve a useful degree of scouring and bleaching. A pad-steam technique can be employed, and offers the possibility of continuous treatment at open width without detriment to the goods. The conditions required are illustrated by the results of a series of experiments in which loom-state rayon-staple cloths were impregnated with peroxide solutions of varying concentration and alkalinity, squeezed so as to retain 1½ times their own weight of liquor, steamed for 2 min., and finally rinsed in hot water. The fabrics employed were light- and medium-weight dress material and a gaberdine, while the peroxide concentration was varied from 0·25 vol. to 1 vol. and the alkali from 0 to 8 g. caustic soda and soda ash respectively per litre. The peroxide solutions contained in addition 5 g. sodium silicate and 0·5 g. Lissapol N per litre.

Removal of starch was poor at all peroxide concentrations when no alkali was present apart from the silicate. Starch removal was only moderate when soda ash was added or with caustic soda concentrations of less than 4 g./litre. With more than 0·5-vol. peroxide and more than 4 g. caustic soda per litre the removal of starch was good. In all cases a substantial improvement in whiteness was obtained at and above 0·5-vol. peroxide concentration.

The general indication was that a good desize and part bleach could be obtained with a peroxide solution of approx. 0·67-vol. strength containing 5 g. caustic soda per litre together with sodium silicate and a detergent. Such a solution is conveniently and economically prepared by dissolution of 5 g. sodium peroxide per litre without addition of a neutralising agent. Samples of the gaberdine material were pad-steamed with the solutions indicated in Table V and then compared for fluidity and starch removal. As in the previous experiments, the liquor ratio was 1·5 : 1 and the steaming time 2 min. Starch removal was good in all cases, except with Solution F, which gave a poor result.

		TABLE IV			
Sample		Composition of Solution (g./litre)			Fluidity
	Na_2O_2	NaOH	Na_2SiO_3	Lissapol N	
Untreated	–	–	–	–	7·5
A	4	–	5	0·5	8·6
B	5	–	5	0·5	8·3
C	6	–	5	0·5	9·1
D	8	–	5	0·5	10·2
E	10	–	5	0·5	11·1
F	–	5	–	–	7·6

Up to 6 g. sodium peroxide per litre the rise in fluidity is slight, and it would appear that a pad–steam treatment with Solution B might be of practical value for the desizing and part bleaching of spun rayons. The material so treated had an attractively soft handle and could be dyed very satisfactorily in a laboratory molten-metal dyeing machine.

Similar work has been carried out on cotton materials, and it is found that these also can be effectively desized and part-bleached by a short pad–steam treatment with sodium peroxide solutions of 10–15 g./litre concentration containing 5 g. sodium silicate and 0·5 g. Lissapol N per litre without increasing the fluidity above 4·0.

Wool

A large proportion of woollen and worsted goods are either finished in the natural colour or dyed without bleaching. Bleaching is, however, required for such materials as white knitting yarn, white flannels, fine hosiery, blankets, and also as a preliminary to dyeing in pale colours. In addition there is a limited amount of part bleaching of raw wool in' scouring ranges.

Formerly woollen goods were bleached by the sulphur stoving process, in which the moist material is subjected to the action of sulphur dioxide derived from burning sulphur, approx. 6 lb. of sulphur being required for 100 lb. of wool[37, 38]. A moderate degree of bleaching is obtained with good handle and lustre, but the colour is not permanent and the process has many practical disadvantages. It has now been largely superseded by peroxide treatments, which give a better and more permanent white. Sulphur stoving is still carried out to a limited extent, sometimes after a peroxide bleach because it further improves the colour and the lustre of the wool. Residual traces of sulphur dioxide in the goods are liable to give rise to an unpleasant smell on ageing, but this can be avoided by means of a final rinse in water containing approx. 0·25 g. of sodium perborate per litre. Variations of the sulphur dioxide bleach have been put forward, particularly the use of an acidified solution of sodium bisulphite[39] and the use of a 2 : 1 mixture of sodium bisulphite and sodium sulphite at pH 6·8[40]. These processes are still employed to a certain extent.

Peroxide bleaching of scoured yarn and hosiery is usually accomplished at pH 8–10 with a 1·5–3-vol. solution of hydrogen peroxide containing per litre 2–3 g. of stabiliser, which may be sodium silicate or sodium pyrophosphate. If sodium silicate is used, the goods must receive a very thorough rinsing to ensure a soft handle, and hence in practice sodium pyrophosphate is generally preferred. In this particular type of bleach at moderately low temperature sodium pyrophosphate is a satisfactory stabiliser, but for high-temperature peroxide bleaching, as in the case of cellulosic textiles, it is essential to use silicate.

Bleaching is carried on for 3–5 hr. at 120°F. and is sometimes followed by treatment with reducing agents such as sodium hydrosulphite (dithionite) solution (2 g./litre) to raise the whiteness further. The strength of the peroxide bath falls by only 20–30%, so for economy in working the bath is usually retained and refreshed for succeeding batches of wool by suitable additions of peroxide and stabiliser. Hosiery fabrics are treated in stainless-steel winch machines, and half-hose in paddle machines. Yarn is bleached on hank in Hussong-type machines or in vats made of wood, tile, or stainless steel, and also in package form in dyeing machines.

Bulky piece goods such as blankets are occasionally bleached on winch machines, but more commonly by semi-continuous processes in which the goods are saturated with a 4–6 vol. peroxide solution and piled for approx. 24 hr.

In this type of process the peroxide solution may be either acid or alkaline, as distinct from the immersion processes, where alkaline solutions are normally required for satisfactory bleaching.

In operating the semi-continuous process under alkaline conditions sodium silicate is added to the peroxide solution in the proportion of 5 g./litre, and the bleaching solution is applied at a temperature of 110–120°F.

At the end of the piling period the material may be dried without rinsing, but to obtain the best results in subsequent raising operations it is preferable to rinse and acidify before drying.

In the acid process the peroxide solution contains 2·5 g. formic acid per litre and is applied at room temperature[41]. The degree of bleaching is substantially the same in both cases, but the acid process is claimed to have the advantage that rinsing is not required and there is no tendency for bleeding of coloured headings. A certain amount of bleaching may be obtained in a fully continuous process in which either the acid or alkaline peroxide solution is applied and the material is passed straight into a drying machine. The results are, however, much inferior to those given by the semi-continuous process involving piling. Nevertheless, a fully continuous treatment involving saturation with acidified hydrogen peroxide solution followed immediately by drying is in fact employed on loose wool for improving the colour somewhat[42]. An extra bowl made of stainless steel is fitted at the end of a normal raw-wool scouring range and is used for impregnating the fibre with a 1–3 vol. peroxide solution at room temperature, the pH being maintained at 4–6 by addition of sufficient sulphuric acid. The wool is squeezed and then dried immediately at temperatures not exceeding 200°F. for approx. 7 min. Reversion of colour during subsequent dyeing can be avoided by drying at the lowest practicable temperature and ensuring that no residual hydrogen peroxide remains in the wool, either by ageing for at least 48 hr. before dyeing, or by adding a small amount of reducing agent such as sodium hydrosulphite to the dyebath[42]. Ageing is preferable, because the colour of the wool· continues to improve for 24–48 hr. after drying.

Highly pigmented wools and hairs such as Karakul, cashmere, and alpaca are also bleached by peroxide processes, but present great difficulty. The best that can be obtained without detriment to the fibre is a pale fawn, and even then it is necessary to activate the peroxide solution by addition of potassium or ammonium persulphate or else to mordant the fibre with iron salts before peroxide treatment.

Regenerated protein fibres are bleached by peroxide processes similar to those employed for wool.

Synthetic Fibres

Nylon is sometimes yellowed during dry heat-setting, and to restore the original whiteness it may be necessary to carry out a bleaching process after scouring. Sodium hypochlorite has no bleaching action on nylon, and the best results are usually obtained with sodium chlorite at a concentration of 0·5–1·0 g./litre in the presence of formic, acetic, or nitric acid at pH 2·5–3·5 and at 150–200°F. Bleaching is completed in 30–60 min., and the addition of a sulphated fatty alcohol (1–2 g./litre) can be advantageous, because the foam tends to reduce the evolution of chlorine dioxide fumes.

Hydrogen peroxide at 1–2 vol. strength can be employed in the presence of sodium silicate (3 lb./100 gal.), but the temperature of bleaching should not exceed 130°F. or the nylon may be weakened. Bleaching is completed in 2 hr., and the baths can be refreshed and used again.

Peracetic acid has been suggested as a bleaching agent for nylon at pH 4–6 at 0·5-vol. strength, and this solution is less corrosive towards stainless steel than is sodium chlorite. Bleaching takes place in 30–60 min. at 120°F.

Polyester fibres such as Terylene may be bleached, if required, by sodium chlorite, brought to pH 2–3 with nitric acid, for 20 min. or longer at 205°F.

Polyacrylonitrile fibres such as Orlon are turned yellow by alkaline scouring agents, and therefore neutral detergents should be employed at 160–180°F. Bleaching can be carried out by treating with 1% oxalic acid at 195–212°F. for 30 min., and a further improvement in colour is sometimes obtained by bleaching with sodium chlorite as suggested for polyester fibres.

Orlon and Terylene are sometimes bleached with neutral or acidified solutions of sodium hypochlorite.

Broadly speaking, the general trend during the past ten years in bleaching all types of materials, as in every branch of the industry, has been to increase mechanisation by using new and improved

machinery and techniques to offset the rising labour charges, while the cost of the actual chemicals used has become relatively of less importance than in the pre-war era.

TECHNICAL SERVICE DEPARTMENT
   BLEACHING SECTION
      IMPERIAL CHEMICAL INDUSTRIES LTD.
         GENERAL CHEMICALS DIVISION
            WESTON POINT
               RUNCORN
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Discussion

Mr. S. BURGESS: Whilst not much engaged in bleaching as such, my firm are called upon to supply so-called whites on various man-made fibres, and we are somewhat concerned that there is apparently no agreement as to what constitutes a good white. Some patterns are so heavily tinted

that they can more accurately be described as pale greys, and others, owing to an excess of fluorescent brightening agent, are pinkish. Can the authors offer any guidance?

Mr. WHITE: A standard white should have 100% reflectance at all wavelengths throughout

the visible spectrum. This is never attained in practice, and we consider that a good white should have 90–95% reflectance at 4700 A. before application of any tinting or fluorescent brightening agents.

Mr. J. GREENWOOD: Do the authors know of any method of distinguishing between hypochlorite and peroxide bleaching, other than the aniline pinking test?

Mr. WHITE: No other method is known, but in view of the fact that peroxide-bleached cotton sometimes has a higher wax content, determination of the latter may give some indication. It must be emphasised, however, that the wax content is primarily dependent upon the nature of the scouring operation rather than the use of any specific bleaching agent.

Mr. GREENWOOD: In bleaching yarn by the peroxide process for surgical dressings, a high degree of absorbency is required. How can this be achieved whilst retaining the essential softness of the yarn?

Mr. WHITE: For a given standard of absorbency the softness of the yarn can be improved by avoiding unduly high pH values in the peroxide bleach and by rinsing thoroughly with hot water to remove all silicate. The addition of Lissapol C (ICI) to the bleach bath is also found to be advantageous.

Mr. C. P. ATKINSON: The English shortened bleach procedure using J boxes in desizing and chemicking and using auto-piled waggons in connection with the Mather waggon kier is essentially a continuous procedure. 'n judging the merits of kier boiling followed by hypochlorite bleaching relative to the continuous peroxide system advocated for cotton fabrics and without having to resort to the use of fluorescent brightening agents, consideration has to be given to (a) the quality of the cotton available, (b) the degree of permanency of the white required, and (c) the end-use of the fabrics in question.

Mr. CROWDER: The shortened process in question is not in fact fully continuous.

Mr. J. PORTER: What is the highest temperature than can safely be used in the hypochlorite treatment of kier loads of linen and cotton piece goods?

Mr. WHITE: The results given by Derry [43] show that temperatures of up to 60°C. can be used safely for bleaching cotton with sodium hypochlorite. Bleaching is very rapid at elevated temperatures, and the time of treatment must be accurately controlled to avoid degradation of cellulose. In practice, this would be extremely difficult when handling kier loads of piece-goods unless J boxes, Gantt pilers, or other special equipment were employed so that the cloth could be run continuously.

Mr. H. R. HADFIELD: Have attempts been made to "flash-bleach" fabrics by the action of oxygen-liberating catalysts either before or after the application of the bleaching agent?

Mr. WHITE: The only known application of this technique is in the bleaching of highly pigmented fibres such as cashmere and fur, where the material is sometimes mordanted with iron compounds before immersion in a peroxide bleaching bath.

Dr. P. F. PASCOE: What difference does the application of sequestering agents make to the efficiency of the peroxide as well as to that of the hypochlorite bleach?

Mr. CROWDER: Metal-sequestering agents can be useful in peroxide bleaching baths for avoiding stains and in preventing catalytic decomposition of the peroxide. In normal circumstances addition of sodium silicate confers adequate stability, particularly if traces of magnesium salts are present in the water supply or are deliberately added to the bath. Occasionally a sequestering agent is used instead of silicate in a short peroxide bleaching treatment given to cotton yarn prior to dyeing.

Dr. PASCOE: What anti-chlors are actually used? I would like to know whether hydrazine hydrate has been used for this purpose. This chemical should show considerable advantages over sulphites and similar compounds, as it leaves no solid residues behind.

Mr. CROWDER: The usual anti-chlor agents are sodium bisulphite, sodium sulphite, and sodium thiosulphate. Peroxide baths are also anti-chlors. We have never heard of hydrazine hydrate being employed.

Dr. P. W. CUNLIFFE: It is desirable that the composition of the silicate should be stated. Does the quantity of SiO_2 in the peroxide bleaching bath affect the bleaching process?

Mr. CROWDER: Grade J 81 sodium silicate (ICI), which has a very low iron content, is specially prepared for use in peroxide bleaching. It is a mobile liquid which is easy to handle and has a ratio of SiO_2 to Na_2O of 2·5 : 1. Experiments have shown that the quantity of SiO_2 in the bleaching bath is not as critical as the actual pH value of the bleaching solution.

Mr. R. W. SPEIRS: It was stated in the paper that the use of sodium hypochlorite reduces the amount of acid required for souring. Is this established fact? Also that the use of sodium hypochlorite allows sulphuric acid to be used instead of hydrochloric acid. What is the objection to the use of sulphuric acid after a calcium hypochlorite bleach? We know from school chemistry that calcium sulphate is "insoluble", but at the concentrations used in bleaching and with the lavish amounts of wash-water subsequently used, any calcium sulphate formed will be readily dissolved.

Mr. WHITE: In practice it is found that less acid is required for souring when sodium hypochlorite is employed. It is true that calcium sulphate is slightly soluble in water, but in practice it is found that after a calcium hypochlorite bleach a sour with hydrochloric acid gives a softer handle than a sulphuric acid sour.

Mr. SPEIRS: In chlorite bleaching the authors recommend tiled vessels with the tiles set in rubber latex. Is not rubber attacked by chlorite? What life would be expected from such plant?

What is the maximum temperature at which the pad–steam process could be operated in such plant?

Mr. WHITE: Sodium chlorite solutions attack vulcanised rubber, and the sulphur present causes catalytic decomposition of the chlorite. This does not apply to the special cements containing rubber latex, where no sulphur is present. We have a tiled-lined pot which has been in use for chlorite bleaching for several years; the tiles are set in rubber latex cement (Semtex), and the cement shows no sign of deterioration.

In the pad–steam process the chlorite solution can be applied cold, and the cloth then steamed at 100°c.

Dr. C. A. MUHR: With new machinery and by application of superheated steam (Dungler system) desizing, boiling off, and bleaching can be done as a continuous process in very short time. Sodium chlorite can be applied in a most economical way without any danger of corrosion. Chlorite seems to be the best product to remove "flecks". In the Dungler method the steam consumption is reduced to a minimum. The quality, especially in linen bleaching, is extraordinary. Heavy fabrics can be bleached in 14–20 min.

Mr. G. B. ANGUS: Have the authors any information on the respective losses of substance incurred in the various bleaching processes?

Mr. WHITE: The main loss in weight in cotton bleaching occurs in the scouring stage, and therefore if a thorough scour is given, the loss in weight will be of the same order whether hypochlorite, peroxide, or chlorite is used in the actual bleaching. Peroxides and chlorite can be used after a mild scour or even without any prescour, and in such circumstances the loss in weight is correspondingly reduced, especially in the case of chlorite bleaching.

Mr. ANGUS: What are the respective costs of the various methods of bleaching discussed in the paper?

Mr. WHITE: We would rather not comment on the relative costs of the various methods of bleaching, because the cost depends upon many factors other than the cost of the chemicals.

Mr. J. W. REIDY: Would the authors comment on the value of the alkali solubility test as a routine test in linen bleaching as compared with the use of fluidity tests?

Mr. CROWDER: The fluidity test has the advantages of being more closely related to the intrinsic strength of the linen and of being more sensitive in the initial stages of chemical degradation. The greater sensitivity of the fluidity test is particularly apparent in cases of oxidation with acidified solutions of hypochlorite such as are employed in linen bleaching. An example of this was encountered in the case of a linen yarn which had a solubility number of 2·0 and a fluidity of 3·0 after scouring, but after subsequent bleaching the solubility number was only 3·0 whereas the fluidity had risen to 9·0 and the yarn gave a reaction for reducing oxycellulose in Harrison's test.

The fluidity is a measure of the average chain length of the cellulose molecules, whereas the solubility number determines only the proportion of chain molecules below a certain length.

Mr. F. CHAPMAN*: There are no references in the paper to bleaching agents such as N-chloro compounds, e.g. dimethyldichlorohydantoin, or to lithium hypochlorite. Both compounds are claimed to give excellent bleaching with minimum fibre tendering. Have the authors any experience of the performance of these particular materials in continuous or ordinary bleaching processes?

Mr. WHITE*: The bleaching properties of dichlorodimethylhydantoin have been examined, and it is correct that this substance has on the whole rather less tendency than hypochlorite to degrade cellulose. The general performance, however, does not appear to be commensurate with its probable cost. The same is probably true of lithium hypochlorite, although both substances may have advantages as household bleaching agents, in view of their excellent stability on storage and ease of packaging.

Dr. W. HONNEYMAN*: Have the authors considered alternative stabilisers for hydrogen peroxide (apart from silicate). Silicate is objectionable for linen, as silica is deposited in the fibre and leads to a harsh finish and much "fly" on winding, containing a considerable amount of silica. Pyrophosphate was suggested many years ago, but was not altogether satisfactory.

Mr. WHITE*: Sodium silicate is undoubtedly the most effective stabiliser. Pyrophosphate is a satisfactory stabiliser when the temperature is low, as e.g. in bleaching wool at 40–50°c. In bleaching linen, where higher temperatures and higher pH values are employed, it is found that pyrophosphate is much less efficient than silicate and leads to inferior bleaching. We have not found that silicate leads to a harsh finish on linen yarn if there is sufficient alkali in the peroxide bath and if the yarn receives a hot rinse prior to the final cold rinsing.

Mr. W. PENN*: Only passing reference has been made to bleaching with peracetic acid. Peracetic acid is being used in the U.S.A. for bleaching acetate rayon warp–cotton-covered rubber weft fabrics. It is claimed that good seed–mote removal from the cotton is attained without adverse effect on the cellulose acetate component of the fabric. Are the lecturers able to confirm that peracetic acid bleaching is effective for seed–mote removal from cotton?

Mr. CROWDER*: We have not had any experience in the use of peracetic acid for bleaching cotton.

* Communicated

A New Approach to the Continuous Dyeing of Cellulose Fabrics with Direct Cotton Dyes

J. WEGMANN

There are two main reasons why direct cotton dyes are difficult to apply by continuous methods. Firstly, it is difficult to maintain uniformity of colour during the dyeing process because of the affinity of the dye for the fibre. Secondly, direct cotton dyes of good wet fastness have a low rate of diffusion, which means that a longer steaming time is necessary to bring about fixation. It has been found that copper-complex polyazo dyes form loose complexes with certain amines, and that these complexes diffuse rapidly and can be applied evenly to the fibre. These amines are displaced during steam fixation in an ager and are subsequently removed by rinsing, which results in a normal dyeing. This method also permits simple and reliable continuous application of highly substantive direct dyes, such as are to be found in the range of copper-complex products.

Introduction

Apart from the general demand for higher fastness, the main need in textile dyeing today is simpler and speedier methods of application. It has become apparent in recent years that, in oversea countries in particular, the need for rationalised dyeing methods is as urgent as that for improved fastness. Thus, in order to keep pace with the requirements of dye users, research workers must press forward in the search for new dyes and new methods of dyeing. However, developments in methods of application to improve fastness have, hitherto, tended to lengthen and complicate the process of dyeing. In many cases, the prerequisites for high fastness and short dyeing time are diametrically opposed, and it is no easy matter to reconcile them.

In the case of vat dyes, the problem of obtaining high fastness by rapid application has been solved and many firms have gone over to the time-saving continuous processes. There is no doubt that many users of direct cotton dyes are also eager to break away from winches and jigs and to adopt more economical methods of working.

Although much work has been done in this direction, direct dyes have not been able to keep pace with the vat dyes. Many styles which could very well be dyed to the required fastness with directs are now dyed with vat dyes because the advantages of continuous dyeing more than counterbalance the extra cost of the faster dyes.

The drawback in continuous application of direct dyes, as opposed to vat pigments, is that their affinity for the fibre does not permit purely mechanical impregnation. Very pale colours and dyeings not requiring any specific degree of fastness could be an exception in some cases. However, those direct dyes which would really be of interest for present-day mass-produced styles, viz. dyes which combine fastness to light and crease-resisting with good wet fastness, present the greatest difficulties on account of their high affinity and low rate of diffusion.

The purpose of this paper is to suggest a principle which offers the possibility of applying fast direct dyes successfully by continuous methods without in any way detracting from their normal properties.

Earlier Work

In contrast to the great number of papers which have been published on the application of direct dyes in long liquors, and which treat of their diffusion, levelling, and exhausting properties, very little literature has been forthcoming on their continuous application.

G. T. Douglas [1] emphasises the importance of fabrics being thoroughly pretreated, so that they have good absorbency, of using dyes which are readily soluble, and of avoiding electrolytes. High padding temperatures would be desirable to obtain thorough wetting of the material and to ensure higher solubility of the dye, but this would increase the rate of strike. The compromise suggested is to pad at 50–60°c. Thickeners are not advocated, since they impede fixation. On leaving the pad-mangle, the goods should pass directly into a Mather & Platt ager, where they are steamed for 5 min. About twenty dyes of the Durazol (ICI) and Chlorazol (ICI) ranges show satisfactory fixation and normal fastness by this method. It is pointed out that there is no evidence of one or other of the three classes of the S.D.C. classification predominating.

J. A. Woodruff [2], who also classified direct dyes in a manner similar to the S.D.C., claims that "A" dyes are good as regards coverage, depth, and solubility. In the case of "B" dyes, good solubility is an important factor. There is little need of salt, and higher temperatures should be used. However, feeding additions present a problem owing to the differences in exhaustion properties of direct dyes. The same applies to "C" products.

H. Moore and co-workers [3] have made a detailed study of the effect of variables such as temperature, pressure, and speed on liquor pick-up in padding. They also examined the influence of storage before drying, the influence of steaming, and the effect of additions of solubilising agents on fixation of dye. The most favourable padding temperature proved to be 80°c., and 12 hr. at an elevated temperature the most suitable condition of storage before drying. Of the various additions tested, diethylethanolamine was the most effective.

The process is suggestive of the Pad–Roll system [4], in which the material is padded, heated by infrared

lamps, and then batched in a steam-heated chamber. The roll of material is rotated in this chamber for a period of one or more hours. All direct dyes should be applicable by this method. It is, however, not strictly a continuous process, but, in fact, dyes in a liquor ratio of about 1 : 1.

M. R. Fox [5] states that good results can be obtained with direct dyes on a pad–steam range, the goods being steamed for 3–4 min. However, dyes have to be selected carefully.

F. Gund [6] points out that immersion time should be sufficiently long to permit good penetration. This, of course, brings with it a replenishing problem, which, however, is easier to solve when a small bath is used. He recommends a V-shaped trough providing for a 50-cm. immersion length, and a running speed of 30 yd./min. A steaming time of 3–5 min. at 105°C. is generally sufficient.

E. Köster [7] suggests a steaming time of 2–3 min. followed by treatment in a salt bath. A run through a hot salt bath does not lead to good results, especially in the case of full colours, since the dye coagulates on the surface and cannot diffuse sufficiently rapidly into the fibre.

It is important that the dyes used should be free from salt, that they should possess very similar rates of dyeing, and also that the padding liquor should be hot and the trough small.

A. Koch [8] also stresses the importance of working with small troughs, of continually replenishing the liquor, and of working at a speed of 60–90 yd./min. Compared with a jig dyeing, a corresponding pad dyeing does not show normal fastness or normal colour. However, fixation can be improved by steaming for 5 min. at 22 lb./sq.in. If fixation is to be carried out in a salt bath, it must be borne in mind that a relatively long treatment is involved, and this does not permit continuous working. If a pad dyeing has not previously been fixed by salt or steaming, there is no point in aftertreating with Sandofix WE (S) or Cuprofix S (S).

In a paper on the principles of continuous dyeing, W. J. Marshall and R. W. Speke [9] point to the great difference in time of fixation between vat dyes and direct dyes. Whereas the former can be fixed within 30 sec., even selected direct dyes require at least 3–4 min. P. A. Holt [10] also emphasises the considerable differences in time (1–25 min.) required for fixation within the group of direct dyes itself: times vary between 1 and 25 min.

At present only pale to medium depths can be produced continuously by the pad–steam process, and these only with a carefully selected group of dyes which can be fixed rapidly. Another limiting factor is the demand for dyes which withstand crease-resist treatments.

To sum up, it can be said that, for continuous working, dyes have to be selected with considerable care, and that selection is restricted mainly to those products which are less fast to wet treatments and which diffuse rapidly. Goods are best padded at high speed through a short, hot liquor.

If the goods are to be dyed continuously, and development is not to be effected by laying up, on a jig, or by the Pad–Roll system, the best procedure to adopt is a 5-min. steaming. Development in a salt solution is too time-consuming and, in addition, results in a considerable loss of dye; aftertreatment with fixing agents gives poor results.

The Problem in Essence

From the foregoing it can be seen that two main difficulties are encountered in the continuous application of direct dyes—

(1) Change in concentration of the padding liquor due to an affinity factor, the nature of which has not yet been explained

(2) Inadequate fixation in short steaming times due to low rate of diffusion.

The following possible methods of overcoming these difficulties have suggested themselves—

(a) Development of new dyes of good fastness to light and crease-resisting (disregarding wet fastness), and of low substantivity, good solubility, and high rate of diffusion, the normal standard of wet fastness to be produced by aftertreatment with a fixing agent. However, it was not found possible to develop dyes which show a sufficiently high rate of diffusion, and which at the same time can be improved satisfactorily in wet fastness properties.

(b) Temporary modification of the properties of dyes in the aqueous phase. Naturally, a chemical modification similar to that carried out in the case of the solubilised vat dyes could not be considered, since, apart from other disadvantages, it would have meant a further aftertreatment to split off the unwanted groups. The aim was, in fact, to impart to the dye certain properties when in the aqueous bath which it would subsequently lose when fixed on the fibre.

Dyes had to be chosen, firstly whose fastness properties were high enough to warrant modification, and secondly whose structure would permit modification. The water-soluble copper-containing polyazo dyes fulfilled these requirements.

Copper-complex Polyazo Dyes

GENERAL

The discovery that direct dyes could be produced which contained the copper atom firmly bound in the dye molecule was made in the Ciba laboratories in 1915 [11]. Ciba continued to develop these types of copper-complex dye, and the present Chlorantine Fast range contains more than twenty such products. These dyes are among the fastest of the direct dyes. In general, they possess very high light fastness, good wet fastness, and good fastness to crease-resist treatments. On the other hand, they are not sufficiently dischargeable, and some are not very readily soluble. This latter factor would appear to make them unsuitable for continuous application.

All these dyes possess either *oo'*-dihydroxyazo groups, *o*-hydroxy-*o'*-carboxyazo groups, or both together, these groups holding copper firmly bound in the complex. They are water-soluble since they possess a sufficient number of sulpho groups, and are substantive owing to their chemical constitution.

STRUCTURE OF COPPER COMPLEXES OF AZO DYES

Our knowledge of the structure of copper complexes of polyazo dyes containing sulphonic acid groups is still very incomplete, and we have to depend on comparisons with similarly formed simple dyes. P. Pfeiffer [12] was able to show that *oo'*-dihydroxyazobenzene formed a true 1 : 1 copper complex, whose free fourth co-ordination site could be substituted by ammonia. The stability of this copper complex is substantiated by the fact that it forms a monohydroxy complex in caustic potash solution; i.e. an OH group replaces NH_3 [13]. Drew and Landquist [14] isolated a mono-pyridine complex in which the base is very firmly bound—
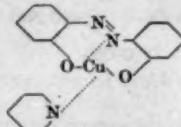
However, as soon as sulphonic groups are present, the structure of these complexes becomes much more complicated, even in the case of mono-azo dyes, and Beech and Drew [15] put forward the following structural formula for the copper complex of 2-aminophenol-4-sulphonic acid→2-naphthol (Copper Red N)—
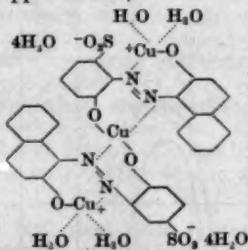

It is thus a 3 : 2 complex, i.e. there are 3 copper atoms to 2 dye molecules, and consequently there are more free co-ordinating sites.

AMINE COMPLEXES OF COPPER-COMPLEX DIRECT DYES

Despite the fact that little is known of the structure of copper complexes of substantive polyazo dyes, it can be assumed that the copper atoms also have free co-ordinating sites which can be saturated. Dye chemists are well acquainted with the fact that certain copperable dyes tenaciously retain ammonia from the coppering solution after metallising. The ammonia is bound within the complex and can be removed by alkalis. On the assumption that the residual valency bonds of the copper atoms provide the linkage with the

cellulosic fibre and also cause the formation of aggregates in aqueous solution, a possibility was seen of temporarily imparting other properties to the dye whilst in solution by blocking these sites. From the application point of view, the problem was to manufacture amine complexes of copper-containing direct dyes which are stable enough not to hydrolyse in aqueous solution, especially at elevated temperatures, but yet are not so firmly united as to prevent the cellulosic fibre from displacing the base to permit adsorption of the dye molecule.

Systematic examination of a large number of amines showed that certain derivatives appear to meet these requirements, particularly amines containing hydroxyl and carboxyl groups—

$$HO \cdot CH_2 \cdot CH_2 \cdot NH \cdot CH_2 \cdot CH_2 \cdot NH \cdot CH_2 \cdot CH_2OH \quad (i)$$

$$HOOC \cdot CH_2 \cdot NH \cdot CH_2 \cdot CH_2 \cdot NH \cdot CH_2 \cdot COOH \quad (ii)$$

$$H_2N \cdot CH_2 \cdot CH_2 \cdot OH \quad (iii)$$

$$CH_2 \cdot NH \cdot CH_2 \cdot COOH \quad (iv)$$

In the above list of bases it may be noted that the last derivative (v)— the well known ethylenediaminetetra-acetic acid— shows such a pronounced tendency to form complexes that it deprives the dye–copper compound of its copper and is thus unsuitable for the purpose.

PROPERTIES OF AMINE COMPLEXES OF COPPER-COMPLEX POLYAZO DYES IN SOLUTION

Solutions of copper-complex direct dyes exhibit different properties in the presence of the above-mentioned amines. The solutions obey Beer's law and are not affected by the addition of electrolytes. Corresponding solutions of the dyes alone, however, become optically denser with increasing dilution as the result of disaggregation; and, when an electrolyte is added, optical density falls because of increasing aggregation, particularly when the solutions are allowed to stand.

In addition to this, solutions of dye mixtures containing amines show additive absorption spectra (Fig. 1), even when one of the components is free from metal. The amine-free solutions, however, exhibit this additivity in very few cases, and then only in complete absence of electrolytes. A possible reason for the non-additivity (Fig. 2) may be that some of the aggregates formed are made up of molecules of both components. As Neale and Stringfellow [16] were able to demonstrate, this non-additivity in the case of mixtures of direct dyes is related to the dyeing behaviour of such mixtures, in that increased modification in absorption spectra is coupled with more marked anomalies in dyeing.

The above findings justify the assumption that copper-complex direct dyes in the presence of complex-forming amines represent true molecular solutions.

TABLE I

Dye I

Dye II

Dye III

Dye IV

Dye V

Dye VI
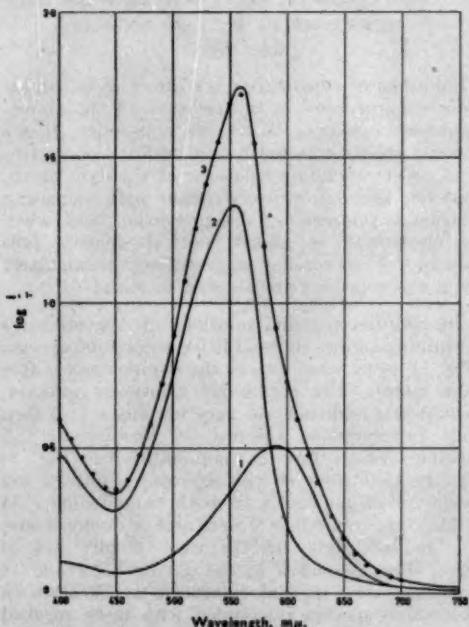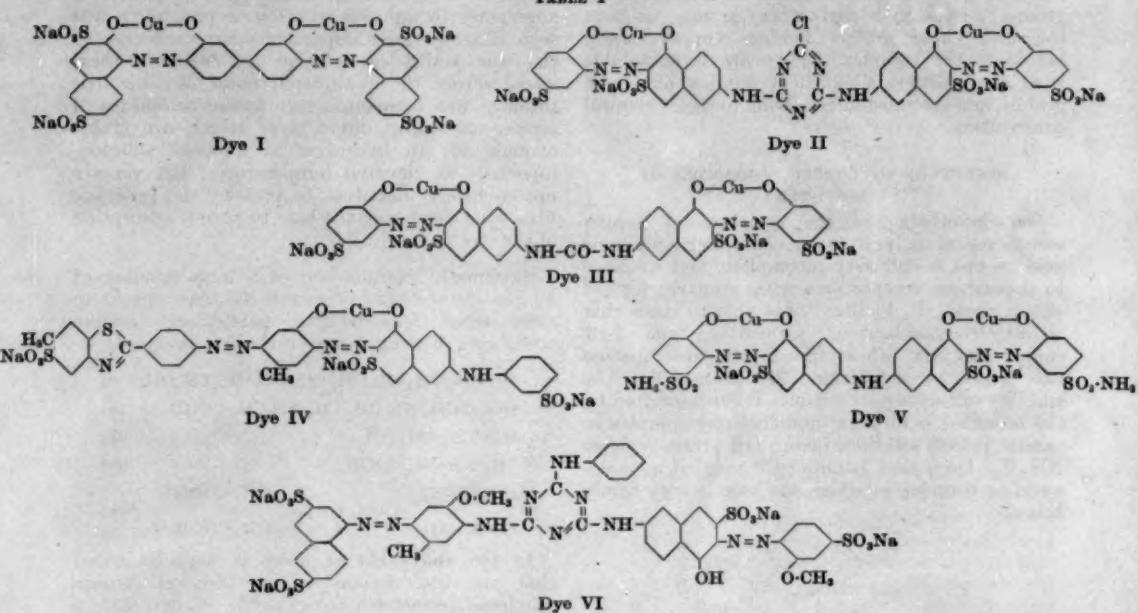
(1) Dye I (Table I)
(2) Dye II (Table I)
(3) Mixture of I and II (1 : 1)
o   Addition of Curves (1) and (2)

FIG. 1— Aqueous Solutions of Dyes containing Amine I (1 g./litre)
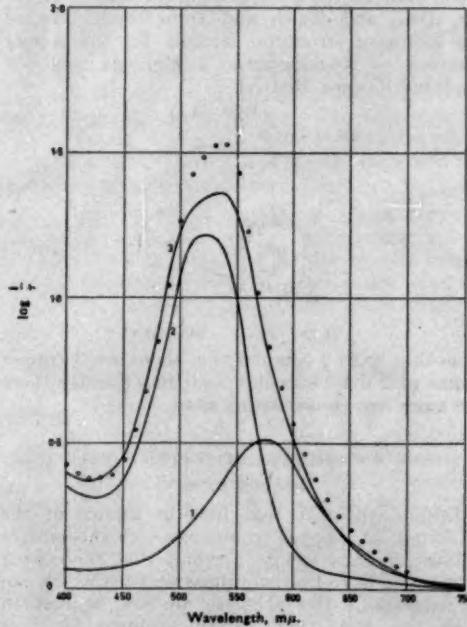
(1) Dye I
(2) Dye II
(3) Mixture of I and II (1 : 1)
o   Addition of Curves (1) and (2)

FIG. 2— Aqueous Solutions of Dyes containing No Amine

(1) Water
(2) Aqueous Amine I (1 g./litre)
(3) Aqueous pyridine (25%)
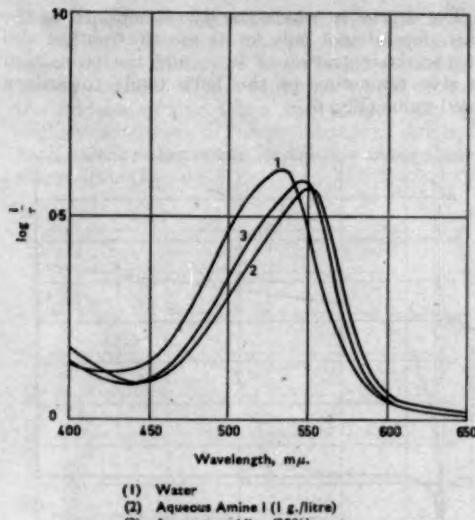
FIG. 3— Solutions of Dye III in Different Solvents

1) Water
2) Aqueous Amine I (1 g./litre)
3) Amine I in absolute alcohol (1 g./litre)
4) Aqueous pyridine (25%)

FIG. 4— Solutions of Dye IV in Different Solvents

Non-metallic dyes can be molecularly dispersed by the addition of pyridine [16, 17], although large amounts are required compared with the small additions of amines needed to produce the same effect with copper-complex dyes. As a rule, with both types of dyes, the absorption peaks are displaced towards the red (Fig. 3) and in some cases the curves change.

Whereas, in the case of copper-containing dyes, low concentrations of pyridine have, with a few exceptions, virtually no effect, larger amounts cause a displacement of absorption peaks similar to that produced by smaller additions of suitable aliphatic amines. Cases have been recorded with metal-free dyes where similar effects could be produced by adding ethylene oxide condensation products, although here, too, larger amounts are necessary (1% solution) to obtain an addition compound [18].

From the fact that, with metal-free dyes, increasing amounts of pyridine bring about a progressive displacement of the absorption peak it can be concluded that a solvatochromic effect is produced. However, when metal-complex dyes are combined with pyridine— and even more so when combined with amine I— there is no comparable dependence on concentration, and this is a further indication that a true complex is formed. Pyridine complexes in aqueous solution appear, however, to be much less stable to hydrolysis, since far higher concentrations of pyridine are required.

Further support is lent to the assumption that a true complex is formed by the fact that various copper-complex dyes which are insoluble in alcohol, e.g. dye IV (Table I), are rendered soluble in alcohol by the addition of amine I or larger quantities of pyridine, and give a spectrum similar to that of the amine complex in aqueous solution (Fig. 4). The corresponding non-metallic dye is not rendered soluble in alcohol, so that any possible salt formation with the sulphonic groups cannot be held responsible for the solubility in alcohol of the copper-complex dye.
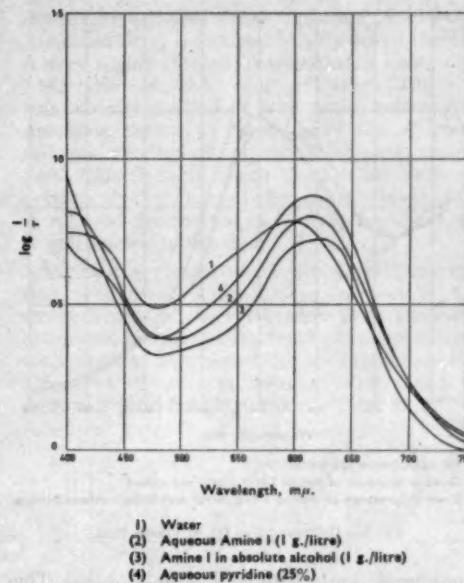
It can be observed that water-solubility of metallised substantive dyes increases considerably on formation of the complex. This could be attributable to disaggregation, since, in contrast to the colloidal solutions of the amine-free dyes, a crystalline precipitate of the dye can be observed in many cases. The crystals are so small and the complexes show such low stability towards hydrolysis that it has not yet been possible to isolate them in substance.

On the strength of these findings we can assume that the bases are added at the free co-ordinating sites to the copper atoms bound in the dye molecule. The blocking of these sites results in the complexes being in a state of true solution, even in high concentrations, and aggregation does not occur even when electrolytes are added.

DYEING BEHAVIOUR OF AMINE COMPLEXES OF COPPER-COMPLEX DIRECT DYES

The dyeing behaviour of amine complexes shows a characteristic change compared with that of the dyes alone, which is in accordance with the changed properties in solution [19]. The differences appear to be of sufficient interest to warrant a description of some experiments, which may make for a clearer understanding of the theoretical aspect of the mechanism.

If a dyeing is carried out with dye V in the presence of amine I (1 g./litre) a much paler colour
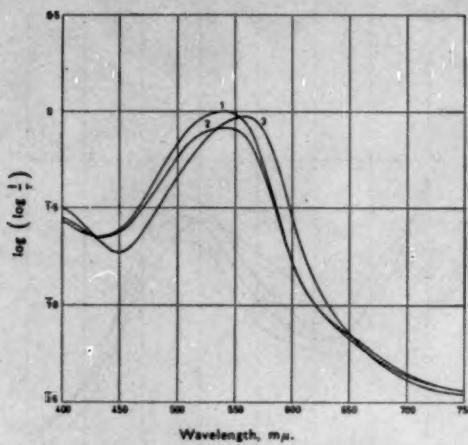
(1) No additions to dye liquor
(2) Dyed in presence of Amine I (I g./litre) and rinsed
(3) Dyed in presence of Amine I (I g./litre) and dried without rinsing

FIG. 5— Dyeings of Dye III on Viscose Film

is produced, both with and without salt. This behaviour is even more pronounced in the case of the less substantive dye III, whereas the non-metallic dye VI shows virtually no reaction to the amine addition. However, the dye fixed on the fibre is in the same state as it would have been if dyeing had been effected without the amine, and, as can be seen in the case of dye III (Fig. 5), the colour turns considerably bluer only when the dyeing is dried without being rinsed, in other words, when the amine remains in the substrate. If the dyeing is dried without being rinsed, the complex is re-formed and remains deposited in the substrate. Normally, however, the amine is displaced when the dye is absorbed by the cellulose, and it remains in the dyebath or is removed by the rinse water.
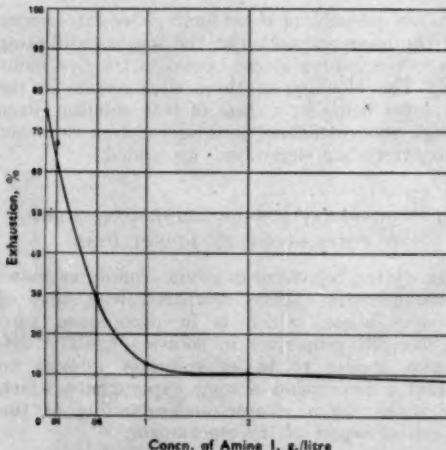
FIG. 6— Dyeing of Dye V (0·125 g./litre; liquor ratio 40 : 1; 2·5 g. Na₂SO₄ per litre; 1 hr. at 100°C.)

The degree to which the dye is retained in the bath depends not only on its constitution but also on the concentration of base, and the proportion of dye remaining in the bath tends towards a fixed value (Fig. 6).

Concn. of Amine
– – – o – – –   0
——o——   0·5 g./litre
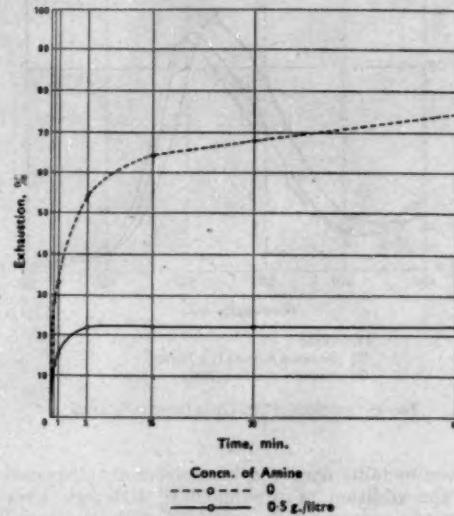
FIG. 7— Dyeing of Dye V (0·125 g./litre; liquor ratio 40 : 1; 2·5 g. Na₂SO₄ per litre; 100°C.)

Concn. of Amine I   Equilibrium Exhaustion at 20°C.
– – – o – – –   0   ● 90%, reached after 38 hr.
——o——   I g./litre   × 38%, reached after 2 hr.
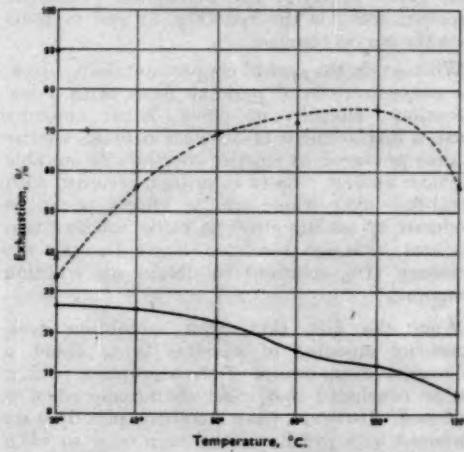
FIG. 8— Dyeing of Dye V (0·125 g./litre; liquor ratio 40 : 1; 2·5 g. Na₂SO₄ per litre; 1 hr.)

As can be seen from Fig. 7, equilibrium is achieved far more quickly in the presence of amine I. This is also apparent from the descending temperature curve in Fig. 8, since it is a well known fact that, at equilibrium, the lower the temperature the greater the dye pick-up. (At

20°c., equilibrium is reached in 2 hr. in the presence of amine I, but in its absence the process takes about 38 hr.)   If the dye concentration is increased and the amount of base in the bath kept constant, the amount of dye taken up changes only very slightly in relation to the percentage of dye in the bath, whereas the curve for the dye alone shows a sharp drop (Fig. 9).

Dye in dyebath, % on wt. of fibre

Concn. of Amine I

--- o --- 0

——o—— I g./litre
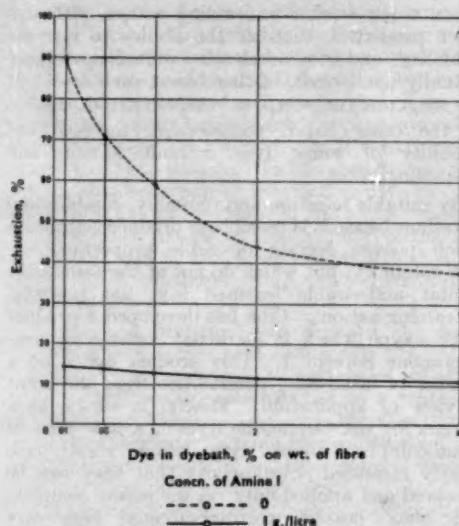
Fig. 9— Dyeing of Dye V (liquor ratio 40 : 1; 2·5 g. Na₂SO₄ per litre; 1 hr. at 100°c.)

Liquor ratio, 10–320 : I

Amine I

--- o --- 0
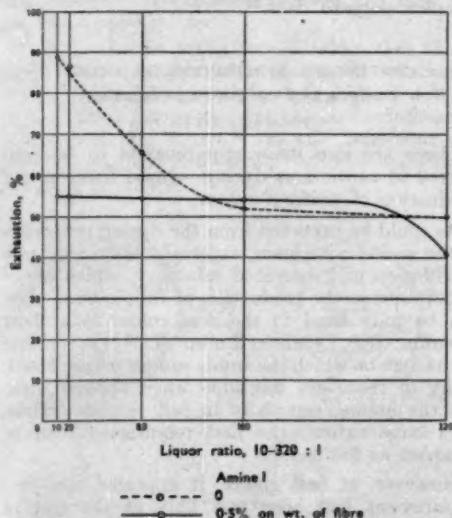
——o—— 0·5% on wt. of fibre

Fig. 10— Dyeing of Dye V (0·5% on wt. of fibre; 2·5 g. Na₂SO₄ per litre; 1 hr. at 100°c.)

The normal dyeing reacts very strongly to a change in liquor ratio, whereas the colour strength in the presence of amine I remains virtually unchanged, provided that the concentration of

electrolyte is based on the amount of dye liquor. A sudden drop is noticeable only when the liquor is very highly diluted, this probably being due to hydrolysis of the complex (Fig. 10).   This behaviour is equivalent to a compensation of the retarding action by increase of the amount of salt (on the weight of the substrate), since the great differences in liquor ratio in the case of the normal dyeing cannot be compensated by an increase in the amount of electrolyte, a fact which is well known to the dyer.

If the dye uptake in relation to salt concentration is followed, a continuous increase in colour strength can be observed; whereas in the absence of amines, the maximum depth of colour is reached with approx. 5 g. anhydrous sodium sulphate per litre, and virtually no increase is recorded when more salt is added (Fig. 11).

Na₂SO₄, g./litre

Concn. of Amine

--- o --- 0
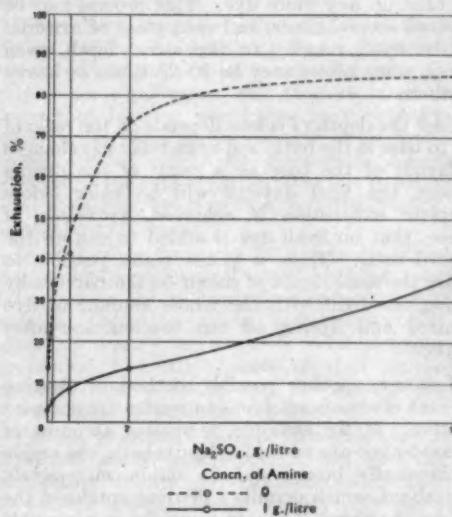
——o—— I g./litre

FIG. 11— Dyeing of Dye V (0·125 g./litre; liquor ratio 40 : 1; 1 hr. at 100°c.)

From these various findings it is evident that the amine complex of the copper-complex dye has dyeing properties differing considerably from those of the same dye applied without the amine. The depth of colour obtainable at a given temperature and with a given concentration of electrolyte is reached very rapidly and depends only on the ratio of dye to base in the bath, within the range in which the complex is stable. The properties of the dyed colour remain the same irrespective of whether dyeing is carried out in the presence or in the absence of the amine.

However, one difference should be stressed: in no case is a bronzy dyeing obtained with amine complexes, whereas in the absence of amine the danger of bronzing increases with increasing depth of colour owing to the tendency of the dyes to aggregate. From the theoretical point of view, this fact may well be of interest in the determination of saturation values of dyes on cellulosic fibres.

From the foregoing it can be seen that the yield obtained with amine complexes can be increased to a certain extent by lowering the temperature and raising the concentration of electrolyte. Nevertheless, a large proportion of the dye remains in the bath. The question thus arises as to what possibilities exist of exhausting the remaining dye.

By way of example, we shall take a dyebath which has been set to produce a 3% dyeing and which, by the addition of amine I, has been adjusted to give only one-tenth of its normal depth. A piece of cotton material is dyed in this bath for 10 min. and a 0·3% dyeing is obtained. A second piece of material is then entered and a 0·3% dyeing is produced on this, too, irrespective of whether it is left in the bath for 5 min. or for 1 hr. As soon as equilibrium has been established, the cellulosic fibre appears to be saturated and does not take up any more dye. This process can be repeated several times, and each piece of material will be dyed roughly to the same depth, even though some pieces may be 10–20 times as heavy as others.

Since the depth of colour depends on the ratio of dye to base in the bath, and since this ratio changes in favour of the base as a result of the dyeing process, the final dyeings will be paler before complete exhaustion is achieved, provided, of course, that no fresh dye is added to restore the original ratio. Thus, it is not really possible to obtain the same depth of colour on ten batches by setting the bath with the whole amount of dye required and dyeing all ten batches one after another.

However, another possible method of clearing the bath of remaining dye is to render the complex inactive. If, for example, increasing amounts of formaldehyde are added to the dyebath, the amine is chemically bound and its action successively neutralised, which permits a gradual uptake of the dye by the fibre. Thus, in principle, it is possible to control the rate of exhaustion by adding specific amounts of formaldehyde to the dyebath.

Since a true equilibrium between amine complex in the bath and dye on the fibre is rapidly established in the presence of amine I, it is immaterial from which side the equilibrium is reached. Thus, it is possible to strip a dyeing by treating it in an amine bath and then cause the same dye to go on to the fibre again by adding electrolyte and formaldehyde. By this process an unlevel dyeing can be stripped and then redyed level without loss of dye.

This method of stripping can be used for assessing dye content, especially as the resulting solutions obey Beer's law. Apart from the fact that the method can be applied only to copper-complex direct dyes, it operates more slowly than the method using 25% pyridine, and is thus of interest in special cases only. (Both methods were used for this work, and no variations were observed.)

Although these experiments, which served to determine the underlying principles of the approach, were carried out with amine I, it must be pointed out that even small changes in the constitution of the amines can have a considerable effect on certain properties. Thus, the following base—

$$HO·CH_2·CH(CH_3)·NH·CH_2·CH_2·NH·CH(CH_3)·CH_2OH$$

has a much more pronounced restraining action than amine I, and the amine—

$$CH_3·C(CH_2OH)_2·NH·CH_2·CH_2·NH·C(CH_2·OH)_2·CH_3$$

has a much weaker restraining action, although other properties, such as the ability to increase solubility and to accelerate diffusion, remain virtually unchanged. Other bases, such as—

$$NH_2·C(CH_2OH)_2·CH_3 \quad or \quad CH_3·NH·CH_2·COOH$$

on the other hand, considerably increase the solubility of some dyes without having any restraining effect.

By suitable selection and, possibly, combination of various bases, it is possible to produce complexes which possess certain desirable properties, e.g. high solubility, but which do not at the same time exhibit undesirable features (e.g. too powerful restraining action). Ciba has developed a product of this type which is marketed under the name Cupranone Solvent I. This product opens up a number of interesting possibilities from the point of view of application. Firstly, it serves as a solvent for the Cupranone dyes [20], a new class of metal-complex direct dyes which show such greatly increased substantivity that they can be dissolved and applied only via the amine complex, and thus possess correspondingly high wet fastness [21]. Secondly, interesting results have been obtained with this product in connection with the continuous application of soluble copper-complex polyazo dyes [22].

CONTINUOUS APPLICATION OF AMINE COMPLEXES OF COPPER-COMPLEX POLYAZO DYES

There are two main requirements to be considered in continuous dyeing—rapid fixation and production of uniform colour.

As could be expected from the dyeing properties of the amine complexes, especially their high rate of diffusion and increased solubility, which are of importance in the production of full colours, they can be fully fixed in the true colour in a short steaming time, i.e. about 2 min. This is in contrast to the dyes on which the amine complexes are based. Many of these are unusable when applied without the amine, especially in full colours. Thus, to a large extent, the first requirement can be regarded as fulfilled.

However, at first glance, it appeared that this requirement had been met only at the cost of greater difficulties in fulfilling the second, viz. uniformity of colour.

The factors governing the reduction in strength of the padding liquor, and hence the variation in colour which occurs, cannot easily be determined experimentally, because examination of reactions between highly concentrated dye solutions and the

fibre substance, which take place within periods of 0·5–3 sec., presents considerable difficulties. Hence, an attempt has to be made to establish these factors by deductive reasoning.

Padding with substantive dyes is accompanied by a greater absorption of dye than corresponds to the amount of liquor padded on, this applying to most substantive dyes. Thus, the colour changes if the feeding liquor is of the same concentration as the liquor in the padding trough. It is very difficult to adjust the feeding liquor and, if adjustment is not effected, the dyer must wait until equilibrium is established and a constant depth of colour obtained. However, since it is not possible to know beforehand exactly how the colour at equilibrium will turn out, it is extremely difficult to dye to pattern. As Marshall [23] was able to show, this behaviour of substantive dyes can be expressed in figures by means of an "affinity factor x". The exact nature of the "affinity factor" is not known, but it has been established that it has no direct connection with the substantivity of the dye.

Boulton and Morton [24] put forward the suggestion that a solution of a direct dye is a polydisperse system consisting of aggregates of dye molecules and single molecules, all in a state of dynamic equilibrium. The condition of this equilibrium depends first on the constitution of the dye and second on its concentration, electrolyte content, and temperature. In the case of dyes of high substantivity the proportion of dye in molecular dispersion is, according to the above authors, extremely small. Although these postulates cannot be proved conclusively, they agree with the phenomena observed and may be regarded as acceptable.

It must also be taken into consideration that, especially in the case of concentrated solutions, dyes are colloidal electrolytes and as such act as salts. Taking into consideration the fundamental work by H. R. Kruyt [25] on the behaviour of lyophilic colloids, we arrive at the following picture (Fig. 12)—
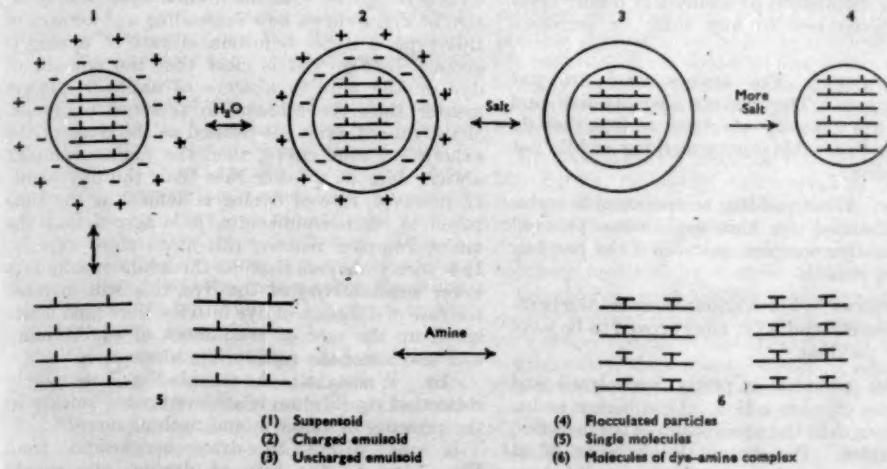
Whereas a normal direct dye may be present primarily in states 1, 2, possibly 3, and, to a very small extent, 5, it is assumed that in the case of an amine complex there is an equilibrium between 5 and 6, which may shift more or less completely in favour of 6 according to the stability of the amine complex to hydrolysis.

When a cellulosic fabric is run through a solution of direct dye, it absorbs the dye liquor and the dyeing process begins. Single molecules diffuse into the intermicellar spaces of the fibre and are adsorbed, whereas aggregates of dye molecules adhere to the surface of the fibre. Hence, the liquor remaining after the run is weaker than the initial liquor by the amount of single dye molecules and aggregates taken up by the cloth. Diffusion of dye molecules is a relatively slow process, whereas the primary adsorption of molecules and aggregates takes place instantaneously: the particles either adhere to the fibre or they do not.

From this it may be concluded that the amount of dye lost by the remaining liquor through diffusion and adsorption of single molecules is of only minor significance, and that an increase in the rate of diffusion would thus have virtually no effect on the reduction in strength of the padding liquor. What might be responsible for this, however, is the primary adsorption due to aggregation, a factor which is not directly related to substantivity.

In view of the foregoing, it was to be expected that amine complexes of metal-complex polyazo dyes—which are molecularly dispersed and thus have no aggregates to be adsorbed—would be taken up evenly in amounts corresponding to mechanical pick-up, in spite of their markedly increased rate of dyeing and the varying degree of substantivity exhibited by dyes.

Various large batches, some of which were dyed under extreme conditions, did, in fact, give highly satisfactory results. Even mixtures containing up to four components of greatly differing substantivity and contrasting hue showed remarkably good uniformity of colour from end to end.

(1) Suspensoid
(2) Charged emulsoid
(3) Uncharged emulsoid
(4) Flocculated particles
(5) Single molecules
(6) Molecules of dye-amine complex

FIG. 12

Thus, the somewhat speculative assumption made at the beginning appears to be justified, and we arrive at the conclusion that amine complexes are particularly suitable for continuous methods of application, not only from the point of view of rapid fixation, but also as far as uniformity of colour is concerned.

As regards dyes suitable for application by this process, it may be said that all direct dyes containing copper bound in the molecule are applicable, i.e. all oo′-dihydroxyazo derivatives, whereas there are certain limitations on the use of o-hydroxy-o′-carboxyazo dyes. Cupranone Solvent I shows such a marked tendency towards complex formation— a necessary property in view of its use with the first-mentioned class— that some of the copper is extracted from certain members of the latter group.

It would appear that excessive molecular size might be a further obstacle to application, since, if dye molecules exceed a certain size, the rate of diffusion is too low to permit full fixation in a steaming time of 2 min., in spite of the dye being molecularly dispersed.

*   *   *

I would like to express my thanks to Dr. K. Menzi for placing at my disposal all the amines used in this work, and for the many valuable suggestions he has contributed.

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Discussion

Mr. A. S. FERN: The amine–dye complex must, presumably, dissociate at some stage of the dyeing process, so that the dye can exhibit its true substantivity. It seems very likely from the constitution of the amines given in the paper that some steam distillation of amine will occur. Has this ever given rise to any toxic or corrosion difficulties?

Dr. WEGMANN: The amines used are not volatile in steam. They are not very alkaline, and in addition are virtually odourless, so that they do not give rise to trouble during working and do not cause corrosion.

Mr. FERN: What padding temperature is normally recommended for this continuous process? Is the amine–dye complex unstable if the padding temperature rises?

Dr. WEGMANN: For various reasons temperatures between 60° and 90°c. have proved to be most suitable for padding.

The amine complex is partly hydrolysed and obeys the law of mass action. Thus higher amine concentrations shift the equilibrium in the direction of the complex. We do not know what effect temperature has on the state of the equilibrium.

It is, however, quite certain that this influence is of little importance compared with the type and the concentration of amine used.

Mr. FERN: It is stated in the paper that the amine–dye complexes have an increased rate of dyeing compared with the normal dye. Examination of Fig. 7 shows how misleading a statement of this type is if no definition of rate of dyeing is given. In Fig. 7 it is clear that the amount of dye on the fibre in absence of amine is always greater than the amount in presence of amine. If the rate of dyeing is defined as the slope of the exhaustion–time curve, then the amine complex always dyes at a lower rate than the dye alone. If, however, rate of dyeing is defined as the time taken to reach equilibrium, it is agreed that the amine complex reaches this state more rapidly. It is surely obvious that, as the amine results in a lower substantivity of the dye, this will increase the rate of diffusion of dye into the fibre (and hence speed up the rate of attainment of equilibrium), and also lower the equilibrium absorption.

Dr. WEGMANN: As regards Fig. 7, we merely state that equilibrium is achieved more quickly in the presence of amine I, and nothing more.

If one wishes to draw conclusions from Fig. 7 as to the rate of dyeing, one should

be perfectly clear in one's mind that the amine complex operates at the saturation limit. That is to say, under these conditions no more dye can be taken up by the fibre, and thus it is not possible to make a direct comparison with the exhaustion of the dye in absence of amine. If a direct comparison is to be made, the correct procedure is to bring both systems to the same exhaustion. This can be done e.g. by increasing the concentration of electrolyte, by decreasing the liquor ratio whilst maintaining the concentration of electrolyte constant, or by increasing the liquor ratio whilst maintaining the same amounts of dye and amine.

The statement made about the rate of dyeing in connection with padding is not misleading no matter what definition of rate of dyeing is adopted, since in the case of the amine complex the amount of dye fixed on the fibre under these conditions (liquor ratio 1 : 1) is always larger. The amine does not reduce the substantivity of the dye and does not bring about any reduction of the equilibrium adsorption; nevertheless, the rate of diffusion is increased. The essential point seems to be that the substance which diffuses is not identical with the substance which is adsorbed. It may be assumed that the amine complex possesses no substantivity and therefore diffuses rapidly. Uptake of dye, however, depends on the relative stabilities of the dye-amine linkage and the dye-cellulose linkage; in the latter case the actual substantivity of the dye comes into play.

Mr. J. BOULTON: The rate-determining process with amine present is clearly diffusion— we have a more soluble, more highly dispersed dye— whereas the rate-determining process for the dye alone is surface adsorption, or strike. With the low degree of exhaustion shown in the first case we have, in measuring time of half dyeing, a fair measure of diffusion rate.

Dr. WEGMANN: I entirely agree with Mr. Boulton's statement.

To minimise the effect of primary adsorption or strike in the absence of amine, comparison with the amine complex must be made in dilute solution (e.g. liquor ratio 160 : 1, see Fig. 10). In this case we find for the latter not only a shorter time of half dyeing but also a higher rate of dyeing, as shown by the slope of the exhaustion-time curve. Generally speaking, this slope does not give a true picture of the rate of dyeing when a marked strike occurs. Cases are known of vat dyes showing, under certain conditions, complete exhaustion in less than one minute, and similar examples can be found with direct dyes. In such cases we cannot really speak of a rate of dyeing, but rather must regard the system as corresponding to padding of the dye from a dyebath on to the cloth.

Mr. C. P. ATKINSON: The production of a pad-steam range is based essentially on the time required for steaming, which is usually of the order of 4–5 min. for direct cotton dyes. The author's conclusion that, generally speaking, amine complexes are particularly suitable for continuous methods of application, giving rapid and uniform fixation in a steaming time of 2 min., is most important in that double the production can be expected for the same range of machinery, or, alternatively, an ager of proportionately lower capacity would meet all requirements— factors of importance to machinery makers and users in view of the appreciable capital expenditure in the plant needed. Apart from the time factor already mentioned, could the author give more details of the conditions of steaming and the construction of the ager proposed?

Dr. WEGMANN: An important point in connection with the time factor is that amine complexes can be padded on to the goods from a hot liquor (70–90°C.), which means that the ager does not have to heat up the goods as well as bring about fixation; when padding with a cold liquor, a large section of the ager has solely this function. Thus, it is essential that the distance between the nip and the ager be as short as possible. The higher the temperature, and the higher the degree of saturation of the steam, the better.

The construction of the ager depends on whether it is to be used for goods dyed with one or several classes of dyes, e.g. vats and directs.

In my opinion, it would be more advantageous to employ the normal type of ager used in pad-steam ranges (about 30 sec. steaming time) instead of an enlarged air-free ager, which is very expensive. A simple ager should be added (principle of enclosed booster with capacity of about 60 yd.). This unit could be used as an additional ager for dyeing with direct dyes and, when dyeing with vats, it would do good service in developing the colour (impregnation with soap solution and developing in a steam-air atmosphere).

Mr. H. A. TURNER[*]: This is not really a question to Dr. Wegmann, but rather to Mr. Atkinson and other textile machinery makers. Do not the present contribution and others on pad-steaming methods for dyeing— especially of direct dyes— suggest that, before the methods can become popular, smaller, lighter, and less expensive steamers than the large festoon types inspired by printing practice must be made available? Could, for instance, drum driers of the Buti type, with suitably modified outer walls and with forced circulation of steam instead of air, make a useful contribution?

Dr. WEGMANN[*]: I am in full agreement with Mr. Turner, especially with regard to machinery used in Britain and on the Continent. This was hinted at in the experiment in which a batch was developed in two passages with direct steam on an ordinary enclosed jig instead of in a salt bath.

I doubt very much whether it would be feasible to modify a drum drier of the Buti type to operate with steam instead of air. If the goods were dyed continuously, the capacity would be restricted by the circumference of the drum, which would be a very short length indeed. In addition to this, two-sided effects would occur owing to one side of the cloth being in contact with the blanket.

* Communicated

The idea of using an enclosed booster, or two in tandem (120 yd. capacity, steaming time of 2 min. at speed of 60 yd./min.), seems to me to be more practicable.

Dr. N. LANDQVIST: From the experimental results given in the paper no definite conclusions can be drawn as regards the state of the dye solutions. It can only be postulated that the dye aggregates are comparatively small and uniform, but the number of molecules in each aggregate is not known. However, studies on this subject, also including comparatively concentrated solutions, can be made by means of free diffusion, and Dr. Wegmann is asked whether such experiments have been carried out.

For measurements of diffusion constant at low concentrations, polarography seems to be a valuable tool. Comparisons made between the polarographic diffusion constants and the corresponding data from free diffusion show that close agreement is present in the case of five direct dyes studied. However, it is necessary in such measurements to ensure that the current obeys the Ilkovič equation as regards the influence of the capillary characteristics, i.e. that no kind of catalytic current is present. From an analysis of the curve shape, a check on the presence of electrophoretic effects can be made; i.e. to find the minimum salt concentration suitable for the measurements.

Dr. WEGMANN: The only indication we have that amine complexes are molecularly dispersed in high concentrations and at high temperatures is that, as a rule, they precipitate as needle-like crystals when the solution is cooled down, whereas dyes in absence of amine precipitate as amorphous flakes.

We have carried out diffusion measurements by various methods, without, however, arriving at anything more than qualitative results. Measurements of free diffusion are not easy to carry out in the case of concentrated solutions and at high temperatures, and evaluation of the results is even more difficult, especially when working with polydisperse systems such as solutions of direct dyes, where there is a much higher concentration of molecules along the diffusion front. The matter is even more complicated in the case of the amine complexes, since they obey the law of mass action. Thus, apart from the amine complex, a certain proportion of free amine, free dye, and possibly dye aggregates are present.

I am afraid that I am not in a position to say to what extent polarographic diffusion constants could be useful in this respect.

Dr. F. C. WOOD: Dr. Wegmann has given us a great deal to think about in his novel paper. I should like him to give us a little of his mental processes which led him on to this line of work, and in particular what led him to choose the particular Amine I—

HO·CH₂·CH₂·NH·CH₂·CH₂·NH·CH₂·CH₂·OH
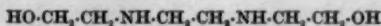
which appears to be the best one for forming his polyazo dye complexes.

Dr. WEGMANN: The idea of making insoluble copper complexes of polyazo dyes directly applicable, instead of producing them on the fibre by aftercoppering, is as old as this range of dyes itself. It was found that amine complexes offered a possibility of solving this problem, and all possible amines and dyes were systematically examined. It was only logical that the action of amines should also be studied on soluble dyes, particularly in order to arrive at an understanding of the mechanism.

The powerful restraining action which was observed was at first considered only as a curiosity. The fact that this system operates at the limit of saturation and that in all cases saturation is very rapidly reached pointed to interesting possibilities. The choice fell on amine I because it has a very powerful restraining action and thus appeared to be specially suitable for the task in hand.

The concentration of interest on continuous dyeing is probably best illustrated by the following experiment—

If 100 g. cotton is dyed in a 1000-c.c. bath containing 1 g. dye per litre and another 100 g. is dyed in a bath containing 1 g. dye and 1 g. amine per litre, the second bath, for example, produces only one-tenth of the colour strength normally to be expected, in other words a 0·1% dyeing. One gram of cotton dyed in the same bath is dyed to the same depth, i.e. only one-thousandth of the dye is exhausted. Thus, the cotton takes part quantitatively in the reaction. If 1000 g. cotton is dyed in this 1000-c.c. bath, i.e. at a liquor ratio of 1 : 1, all the dye is taken up, likewise giving a 0·1% dyeing. If a 1% dyeing is required, 10 g. dye per litre would have to be used.

Mr. H. À BRASSARD[*]: It always astonishes me that discussions about continuous dyeing tend to allege that the method is virtually new and that only now are data about dyes, techniques, and machines available for the purpose. May I remind our Continental friends, in particular, that continuous dyeing has been practised in Great Britain for well over half a century. As apart from the processing of aniline black and mineral khakis on piece goods, I refer, of course, to chain warps. I recollect discussing that point at the Blackpool Symposium and the titters with which it was greeted by some members. And I remember Dr. Cunliffe writing, as if in apology, that dyeing chain warps continously was traditional— the very point I had tried to make.

Will not Dr. Wegmann agree that any dyes used for chain warps in one to four or more box machines are also applicable to piece goods, as that is certainly my own experience? I know that chain warps are not so dyed on the Continent, and I recollect that there was only one machine in Germany. One has only to think of the enormous yardage of chain warps dyed in Great Britain with dyes from every group over the years. Direct dyes of various kinds have been used for the purpose, often dyeing and sizing at the same time. A four-draft chain warp, for example, passing

through dye liquor and squeezes shows itself at the second or third squeeze to look almost like a narrow piece or, as a witty Irishman would say, "it is a piece without a weft".

Quite apart from padding, piece goods have been dyed by a continuous process on a variety of machines and in several colours ever since 1919. It was the late Adolf Singer along with my father's and later my chief chemist, Reginald Pendlebury, and myself who started a plant turning out several hundred pieces per week, and this work was possible because it was based on laboratory work done by Cassella, who gave solubility data and so on. And I am sure that those who knew the Continent well will recollect that in Czechoslovakia in the early 1930s pieces were dyed in a variety of shades and full shades of black with direct dyes by a continuous process. 'The essence of success is the correct choice of dyes, a thoroughly sound prepare, correct time and temperature, correct feed and squeeze, correct liquor ratio, and, I submit, the counterflow I rhymed at Blackpool. Does Dr. Wegmann agree?

At Blackpool I also said that the day of the jig and winch was ending, and I recollect the amused smile that comment brought to several members, and that Mr. F. Scholefield suggested, with gentle sarcasm, that I exaggerated the matter. But I did not and do not withdraw a single word, and in all humility I submit that my forecast has proved correct— *vide* the many continuous machines at work. By the way, I have also dyed union piece goods by continuous processes in the early 1930s.

May I submit for Dr. Wegmann's comments that a small chain warp dyeing machine holding only some 1–2 gal. of dye liquor would be an excellent testing apparatus for laboratory, pilot, or even large-scale work, and thus finally evaluate the scientific and laboratory work under practical conditions. Such machines have, as we all know, been used for chain warp dyeing on even the largest scale.

Dr. WEGMANN*: I fully agree. My comment on the last point is that up to now we have preferred using "pieces with a weft" for our trials because they are easier to handle than "pieces without a weft".

• Communicated

The Dyeing of Viscose Rayon Cakes with Direct Cotton Dyes

T. FLANAGAN

The various classifications of direct cotton dyes according to their dyeing behaviour are reviewed with reference to their assistance to the viscose rayon cake dyer in his choice of dyes. The interpretation of the graphical data of the dyeing characteristics of direct dyes and its limitations are discussed with particular reference to the value of this system in the selection of dyes for cake dyeing and the formulation of a suitable dyeing method.

Some reference is also made to the advantages and limitations of high-temperature dyeing using pressurised machines.

The dyeing of yarn in package form had become an established practice in this country at the time of the introduction of the box-spun viscose rayon cake. Yarn dyed in this manner was less susceptible to damage in the wet state than skein-dyed yarn, and this facilitated subsequent winding and processing. The viscose rayon cake was a ready-made package; and therefore the desirability of dyeing yarn in cake form was self-evident. Several types of cake-dyeing machine were introduced and are still extant, all having one basic feature in common, viz. the yarn is held stationary and the dye liquor is circulated through the cakes by means of a pump. In some cases this circulation is unidirectional—from the inside to the outside of the cake—whilst other machines are fitted with a changeover valve enabling the liquor flow to be reversed to give an outside-to-inside circulation also.

The direct cotton dyes were the first to be applied to cakes, and it is safe to say that even today some 90% of dyed viscose rayon cakes are dyed with dyes of this class. The main considerations attendant upon their application are the wide variations in their dyeing characteristics and the difficulty of obtaining a constant liquor velocity for all parts of the cake. The effect of accelerating the liquor flow is to bring the dye molecules in solution into closer proximity to the fibre surface, thus increasing the dyeing rate. There is also an increase in levelling with increased liquor flow, and this factor has been investigated by Armfield[1]. Therefore, the importance of uniform permeability is obvious.

Viscose rayon swells considerably on wetting, and this, combined with the almost parallel wind of the cake, presents a densely packed mass of fibres to the dye liquor, thus making penetration difficult. To promote uniform permeability it is necessary to have cakes of a standard size which fit snugly on to the cake holders; and after thoroughly wetting out, it must be possible to apply pressure to the swollen cakes very gradually in order to minimise the risk of cakes collapsing. Despite these precautions, the cakes, as set up in the machine, are not uniformly permeable, and variations in the rate of liquor flow will occur for different parts of the cake. The greatest velocity is attained over the ends of the cake, and this will lead to irregularity in the uptake of dye during the early stages of the dyeing process.

The degree of irregularity will also depend to a large extent upon the initial dyeing rate of the dye. Those parts of the cake which first come into contact with the circulating dye liquor will be the more heavily dyed, and as the dye liquor finds its way to the less accessible parts of the cake it is progressively exhausted, thus giving rise to irregular dyeing. Therefore, it is necessary for the dyer to have an intimate knowledge of the dyes employed in order to exploit those factors controlling the rate of exhaustion.

As the dye molecules attach themselves to the fibre surface, diffusion into the fibre matrix takes place, the speed of diffusion governing the levelling rate of the dye. Therefore the dyer must also exploit those factors which promote diffusion, viz. high temperature and a minimum of electrolyte to avoid dye aggregation. Dyeing proceeds by this process of absorption and diffusion, the whole system tending to attain a state of equilibrium between dye on the fibre and dye in the surrounding liquor for a given set of dyebath conditions. In the initial stages of cake dyeing there will be a disparity in the amount of dye held by different parts of the cake, but as dyeing proceeds the dye liquor becomes impoverished, and the more heavily dyed yarn will desorb dye to the dye liquor which will be absorbed by the more lightly dyed yarn. Therefore, dyeing differences will level out as equilibrium is achieved, but the time taken for this to happen will depend upon the initial degree of unlevelness, and the dyer must aim at keeping this disparity to a minimum. This can be effected only if he has a fairly detailed knowledge of the dyes which he employs.

CLASSIFICATION OF DIRECT DYES

The individuality of direct cotton dyes with regard to their dyeing behaviour has been the subject of investigation by a number of workers over the past thirty years. In the early days of viscose rayon dyeing, C. M. Whittaker suggested

a classification based on a capillary test as a guide to the selection of dyes which would yield the most satisfactory results in covering up colour differences in yarn of variable dyeing properties. With the advent of cake dyeing, some ten years later, it was apparent that a fuller insight into the dyeing characteristics of direct dyes would be required in order to predetermine which dyes would be suitable for application by this new process. About this time Boulton and Reading [2] published the results of their investigations of the dyeing properties of direct dyes, and suggested a classification based on the "time of half-dyeing". They found that, for the dyes examined, this varied between 0·07 and 280 min., thus indicating the wide differences in behaviour within this class of dyes.

The factors affecting the dyeing and levelling rates of a number of direct dyes on viscose rayon were investigated in the Dye Laboratory at British Enka Ltd. to determine the rate of dyeing and the effects of temperature and electrolyte concentration on exhaustion. Dyeings were carried out on 5-g. hanks of yarn under standard dyeing conditions, but one dyebath variable was changed at a time. The resultant dyeings were assessed against dyed standards, the percentage exhaustion for each dyebath condition was estimated, and from these data a graph was constructed showing the dyeing characteristics of the dye. In these tests a standard depth of 1·0% dye was used, the dyeings being carried out at a liquor ratio of 15 : 1. The salt controllability was determined by dyeing for one hour at 90°c., the dyebaths being set with varying amounts of salt. The optimum salt concentration— which was then used as standard in the assessment of the other variables— was determined by the construction of a salt sensitivity curve, the point at which this curve flattened out being taken as the optimum salt concentration. The levelling rate of the dye was determined by treating dyed and undyed hanks together at 90°c. in blank dyebaths containing the optimum salt concentration for various lengths of time. The amount of dye transferred from the dyed to the undyed yarn was estimated, and a curve constructed of migration against time.

Working independently, the Geigy Co. arrived at a similar system, depicting the dyeing properties of direct dyes on cotton, and subsequently published a very useful book on this subject.

A system of classifying the suitability of direct dyes for viscose cake dyeing was introduced by ICI. This was based on practical dyeing tests on viscose rayon cakes. Cakes were dyed to a 1·0% depth for 2 hr. at 90°c. in a 40 : 1 liquor and in the presence of 10% sodium sulphate. The dyes were classified according to the levelness of the result obtained.

In order to establish some standardised procedure for assessing the dyeing properties of direct dyes, the Society set up a Committee to investigate the problem, and in 1946 it published its findings [3]. It recommended a classification whereby direct dyes were divided into three classes— A, B, C— based on the migration properties of the dyes and their controllability with salt. This classification was also very useful, but it was never intended by the Committee that it should be extended to cover special applications of direct dyes. Cake dyeing is a special application, as can be shown by the fact that, if the ICI classification of direct dyes suitable for cake dyeing is examined, class A, B, and C dyes will all be found in what they refer to as "Group 3", i.e. dyes showing a marked degree of unlevelness, and therefore not recommended.

THE GRAPHICAL SYSTEM

The system of graphical representation of the dyeing properties of direct dyes indicates to the dyer the extent to which he can rely upon the dye to level itself, and to what extent levelness will depend upon his own skill in controlling absorption.
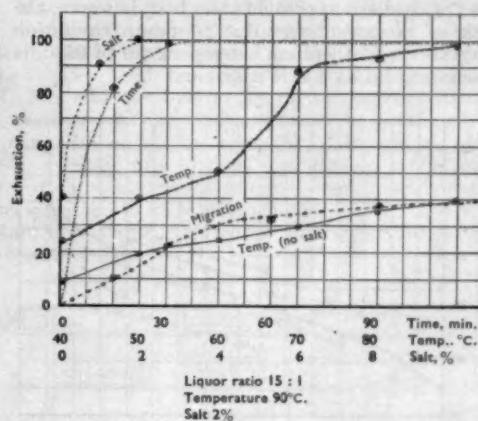
FIG. 1— Cuprofix Red 5BLS

The sensitivity of the dye to temperature and to electrolyte concentration is immediately apparent, thus indicating the form of control which would be most effective, whilst the slope of the curves indicates the degree of control necessary over a particular range of temperature or of salt concentration. For example, in Fig. 1 it is evident that the dye has a rapid rate of strike and that its migration is relatively poor: therefore some degree of control is necessary in order to apply it level. The graph indicates that 40% of the dye will go on to the fibre even in the absence of salt, and that the dye is sensitive to salt addition. For a 1% salt addition a further 50% of dye goes on to the fibre, and the bath is completely exhausted by the addition of another 1% salt. It is obvious, therefore, that the electrolyte addition when using this dye should not be more than 2%, and that the initial feed of salt solution should be made very slowly. It would be safer to make only a 1% salt addition, which would give 90% exhaustion of the dyebath, since the levelling rate is decreased by the presence of salt.

The temperature gradient— in the presence of salt— shows that the critical range is 60–70°c., 40% of the dyeing taking place over this 10°c. rise,

and it is over this range that maximum temperature control should be exercised. In controlling the rate of exhaustion of the dyebath, it would seem logical to take full advantage of temperature control and then to promote exhaustion by the controlled addition of electrolyte. For this reason the temperature gradient which is of more service to the cake dyer is that obtaining when electrolyte is absent from the bath. The graph shows this to be a much smoother curve, and by using temperature control alone 40% of the dye can be transferred to the fibre. As the temperature rises, the dye aggregates or micelles break down in solution, tending to assume unimolecularity near the boil. They are therefore able to diffuse into the fibre more rapidly, and the rate of levelling is increased. This increase in levelling rate with increasing temperature is illustrated in Fig. 2, and it can be seen that it is quite considerable above 90°C. As the dyebath approaches the boil, however, the risk of pressure losses due to pump cavitation increases, and therefore a temperature of 95°C. is recommended as a safe maximum.

solution exhibit all the properties of colloids, and therefore additions of electrolyte cause aggregation of the dispersed dye molecules, which militates against diffusion. The importance of this point is illustrated in Fig. 3, where the amount of dye diffusing from dyed hanks into blank dyebaths set with various electrolyte concentrations has been measured for a number of direct dyes.

FIG. 4— Durazol Brilliant Red BS

Fig. 4 is the graph of the dyeing characteristics of Durazol Brilliant Red BS. This is not a self-levelling dye, but it has a low rate of strike, and both the temperature and the salt sensitivity curves indicate a steady rate of drawing. Since only 12% dyeing takes place in the absence of salt, time would be wasted in exercising temperature control in the case of this dye. The dyeing method here is to commence dyeing at a high temperature and to drip-feed the salt addition from the commencement of dyeing.

With the detailed information furnished by these graphs, the dyer can approach the application of direct dyes to cakes with more confidence, since the degree of control necessary and the type of control which will be most effective are clearly indicated. The optimum drawing temperature will vary from one dye to another, and the graphs will indicate this, thus affording an easy means of promoting the preferential absorption or desorption of a particular constituent of a two- or three-colour mixture to effect matching. It is generally advisable, when dyeing mixtures, to use dyes which have similar dyeing characteristics, but it is often necessary to use non-compatible dyes in order to meet some particular fastness requirement. The dyer who is trained in the interpretation and interpolation of graphical data can predict with a fair degree of accuracy the appearance of his shade at a particular time during the dyeing, and if a correction of shade is necessary, he can assess—in the light of dyebath conditions prevailing at the time— the probability of that correction levelling through within a specified time.

FIG. 2— Increase in Migration at High Dyeing Temperatures

FIG. 3— Effect of Electrolyte Concentration on Desorption

This maximum dyeing temperature having been reached, a carefully controlled salt addition is made to promote an economic level of exhaustion for the dye concerned. The graph will indicate the optimum salt concentration and also the rate at which the addition should be made. This optimum should not be exceeded, because direct dyes in

The graphs are also of assistance in selecting dyes to meet specific wet-fastness requirements. Dyes which have a high affinity in the absence of salt are less likely to bleed than dyes of similar migration properties which are salt-controllable,

but any bleeding which does occur is more likely to produce staining of adjacent white material. Therefore, by a consideration of these properties from the graphical data, the dyer can arrive at an evaluation of the washing fastness for the dyes concerned.

THE RELIABILITY OF GRAPHICAL DATA

For a particular set of dyeing conditions the tendency is for equilibrium to be established between dye on the fibre and dye in the dyebath. Changes in dyeing temperature and in electrolyte concentrations of the dyebath alter the equilibrium level, and these changes are being made throughout the cake-dyeing process. The graphs, however, apply to a fixed set of dyeing conditions applicable to each variable in turn and, therefore, are not truly representative of dyeing practice. To construct a graph which would simulate actual dyeing conditions would involve an infinite number of parameters, which is impossible. Therefore, in applying direct dyes to cakes, some consideration must be given to the probable effect of these changing conditions upon the graphed dyeing characteristics in order to arrive at a suitable dyeing method. Temperature control will be used only with dyes which are not salt-controllable, viz. Class C dyes, and in practice this form of control should be exercised only for the first hour of dyeing. Therefore, the graph of the temperature controllability in the absence of salt will be reasonably reliable for cake dyeing, since dyeing conditions will be similar to those which obtained for the construction of the graph. On the other hand, the salt addition will be progressive and, therefore, not strictly comparable with the salt controllability curve shown on the graph. Experience has shown, however, that the cumulative effect of a salt addition spread over two hours is to achieve a similar degree of exhaustion to that indicated on the graph by an equivalent addition of salt. If the quantity of salt used is less than the optimum, the dye will, of course, continue to exhaust with time, but the rate of build-up will be slow— not more than 10% per hour.

To compare the dyeing characteristics at depths other than the standard (1%), graphs have been constructed for 0·1%, 0·5%, and 2·0% depths. It was found that, for the dyes examined, the variations were well within practical tolerances except for the very pale colours (0·1%). Here the accuracy of the graphs decreased: a greater percentage absorption was obtained in the absence of salt, the temperature control was less, and, of course, the levelling rate was very much less. The practical significance of this is that, when a dye is used in low concentrations as a shading colour, the component dyes will act as electrolyte, and the control of exhaustion of the shading colour will be lost. Therefore it is important to use shading dyes which have a high levelling rate. This is not always possible, but if fastness to washing is the precluding factor, then it should be remembered that Class A dyes have a reasonable fastness when used in

very weak depths of colour. Alternatively, shading dyes should be used which are not salt-sensitive.

In considering the effect of liquor ratio, reference must be made to the trade practice of basing the amount of salt to be used on the weight of material to be dyed. If this basis is used, of course, then shortening the liquor will greatly increase the rate of dyebath exhaustion. However, even when the quantity of salt used is expressed on the sounder basis of concentration in the dyebath, control of exhaustion by both temperature and salt control is less at short liquor ratios, and therefore it is necessary to rely to a greater extent upon the ability of the dye to redistribute itself. The amount of dye absorbed in the absence of added salt is much greater and will depend, of course, on the amount of adventitious salt present in commercial dye powders.

Since levelling depends on diffusion, it would be expected that more levelling would take place from longer liquors, owing to the fact that dye aggregates tend to disperse in dilute solution. This is not found to be the case in practice, and in fact the levelling rate is found to be slightly greater for short liquor lengths. The use of low liquor ratios will effect a considerable saving in steam consumption and enable the optimum dyeing temperature to be attained more quickly. Therefore, on balance, the use of low liquor ratios is recommended.
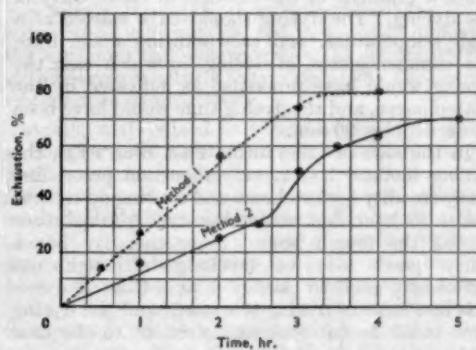

FIG. 5— Exhaustion of Durazol Brilliant Red B 150
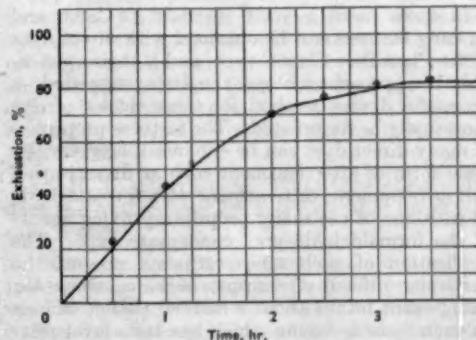
FIG. 6— Exhaustion of Chlorantine Fast Blue FFB

It is not suggested that the graphs will give the dyer perfectly concise information on the behaviour under all conditions of the dyes which he employs, but the fuller knowledge of their dyeing characteristics will materially assist him in their application, enabling him to effect economies both in materials and in dyeing time, and to obtain a higher level of production per machine.

As an example of this, Fig. 5 and 6 show the exhaustion curves of two Class B dyes (Durazol Brilliant Red B 150 and Chlorantine Fast Blue FFB) under actual cake dyeing conditions. Reference to the graphs shows that Durazol Brilliant Red B 150 has little affinity in the absence of salt, that it is very salt-controllable, and that its migration is poor, equivalent to Grade 1 on the Grey Scale for assessing Change in Colour. Chlorantine Fast Blue FFB, on the other hand, shows greater dye absorption in the absence of salt, and it is less salt-controllable than the other dye, but its migration is much better, equivalent to 3 on the Grey Scale. If the same dyeing method is used for both dyes, and in the absence of detailed graphical data the dyer has little alternative, dyeing will proceed as indicated by the continuous line. The method used was to raise the dyeing temperature from 50°c. to 90°c. over the first 30 min., and then to continue dyeing for a further 30 min. before making the salt addition. Since Durazol Brilliant Red B 150 has a low rate of dyeing, this first hour of dyeing time is wasted, as is indicated by the shallow gradient of the exhaustion curve early in the dyeing. The dyeing should have started at a high temperature, and salt addition made from the commencement of dyeing, in which case the dyeing would have proceeded as indicated by the dotted curve, and the dyeing time would have been shortened by 90 min.

In the case of Chlorantine Fast Blue FFB, the dyeing method is correct, exhaustion proceeding fairly steadily for two hours and slowing down over the third hour, but no further dyeing takes place during the fourth hour. Since this dye has a fairly good rate of levelling— although not sufficiently good to classify it as a Class A dye— this last hour of dyeing is wasted, and the dyeing time could be cut without detriment to the final levelness.

AFTERTREATED DIRECT DYES

In most cases a good standard of light and washing fastness can be obtained with direct dyes of the Class B or Class C type, and if their application is approached along the lines suggested, a successful dyeing method for these classes of dye can usually be formulated. The fastness properties of many direct dyes can be enhanced, however, by some form of aftertreatment such as diazotisation and development, or treatment with formaldehyde or with one of the many proprietary fixing agents of the formaldehyde–urea condensate type. The application of such aftertreatments presents no particular difficulty, except, perhaps, when the fixing agent brings about a marked change of hue. In such cases a dyeing which has been level prior to fixation can become distinctly unlevel after fixation, owing to preferential absorption of the fixing agent by the more accessible parts of the cake.

More important as a class, perhaps, are those direct dyes which form a copper complex on aftertreatment with copper salts. In the main these are Class B or Class C dyes, and are applied as the normal direct dyes, but some are of low solubility and precipitate rather easily on the addition of electrolyte, giving rise to dyeings of poor rubbing fastness. Care in the dissolution of such dyes and in the controlled addition of electrolyte will eliminate troubles of this nature.

HIGH-TEMPERATURE DYEING

In dealing with the question of cake dyeing, the methods of approach suggested have been based on the assumption that the normal, unpressurised type of dyeing machine is used. During recent years the pressurised type has been introduced, enabling dyeing to be carried out at temperatures above 100°c. These elevated temperatures give rise to changes both in the hydrodynamic conditions of dyeing and in the behaviour of the dyes themselves. At high temperatures the viscosity of the dye liquor is much lower, and owing to its increased mobility high liquor flow is obtained whilst the pressure across the cakes is low. This results in less distortion of the cake, with a consequent improvement in winding properties.

High temperatures also favour the increased mobility of dye molecules in solution, the diffusion rate is greatly increased, and even the Class C dyes will migrate very easily, behaving in a similar manner to Class A dyes. Additions of electrolyte do not have such a marked effect as in the case of dyeing at lower temperatures, and, owing to the fact that dyeing equilibrium is reached very quickly, it is not necessary to exercise the same rigid control of salt additions. Therefore, the graphical data which are applicable to normal dyeing will not apply to high-temperature dyeing. Nevertheless, direct dyes still retain their individuality in dyeing behaviour at high temperatures, and an unbalanced mixture dyeing will show variations in the degree and rate of exhaustion of the constituent dyes.

The range of direct dyes which can be applied by this process is limited by the decomposition of many dyes at the temperatures employed. In some cases this decomposition can be prevented by adjustment of the pH conditions of the dyebath with ammonium sulphate, but this expedient has only a limited application. A great deal of work has been carried out on this subject, and the results have been published in the literature. Perhaps the most notable contribution was made by Butterworth [4], who compiled a list of dyes which were stable to high-temperature application.

Using pressurised equipment, level dyeings can be obtained with Class C dyes in one hour, and it is claimed that once a recipe has been established, repeat dyeings are extremely consistent in colour, batch-to-batch variation being negligible. However, owing to the limitations enforced in choice of

dyes, high-temperature dyeing of viscose rayon cakes can only be regarded as complementary to the established method of using non-pressurised machines.   *   *   *

The author wishes to express his thanks to the Directors of British Enka Ltd. for permission to publish this paper.

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(*MS. received 30th April 1955*)

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Discussion

Mr. J. GREENWOOD: The author does not state whether he used highly concentrated dyes, such as have been recommended for viscose rayon dyeing.

Mr. FLANAGAN: The answer to this question is really contained in a consideration of the graphs. In the case of dyes which are very salt-sensitive the more highly concentrated dyes should be used, but in the case of dyes which have little affinity in the absence of salt the use of concentrated brands assumes less importance.

Mr. GREENWOOD: What experience has the author had in the use of copper-fixing agents on dyed rayon cakes? Has he found that preferential absorption of the copper complex takes place on the inside of cakes, as has been experienced on cotton cheeses?

Mr. FLANAGAN: The quantities of fixing agents recommended by the dyemaker are adequate to effect fixation. With some dyes this is accompanied by a marked change in shade, and if increased quantities of fixing agent are used further changes in shade occur, although they are not necessarily accompanied by an increase in fixation. Preferential absorption will take place on those parts of the cake which are more accessible to the fixing agent, and therefore if dyes are used which change shade considerably upon fixation, colour differences will occur between the inside and the outside of the cake. Many dyes, however, do not show this avidity for the fixing agent, and the change in shade reaches a definite "end-point". These dyes are quite suitable for cake dyeing. We dye the copper-complex-forming dyes regularly and in large quantities without difficulty.

Mr. J. BOULTON: It is encouraging to hear a dyer with the experience of our lecturer urging the two important facts: firstly, that higher dyeing temperatures encourage levelling; and, secondly, that salt control is essential for the uniform adsorption of salt-sensitive dyes. It was upon the rightness of these two postulates that the Society's Direct Cotton Dyes Committee based its original recommendations[3]. I am somewhat surprised that the lecturer should refer to cake dyeing as a special application of the Society's findings. I have found that dye selection on the basis of those findings has been an essential standby over the years, and generally sound for viscose rayon dyed in any kind of package.

Mr. FLANAGAN: I do not wish to detract from the importance of the S.D.C. classification as a general guide to the dyeing properties of direct dyes. I regard the dyeing of viscose rayon cakes, however, as a "special application", because of the density and the low permeability of this form of package. This demands the full exploitation of the dyeing properties of the dyes used in order that level dyeing can be achieved within an economical time. The S.D.C. levelling test is on a pass-or-fail basis, under conditions of electrolyte concentration which may not be used in practice. The system recommended in the paper indicates the amount of levelling which takes place at the optimum salt concentration and is therefore of greater practical importance.

Similarly, the S.D.C. classification indicates that a dye is salt-controllable, but it does not indicate the optimum salt concentration to be employed or the degree of control that is afforded. The graph system does indicate this.

Again, with regard to Class C dyes, since they are neither self-levelling nor salt-controllable, they could be condemned by the dyer as being unsuitable for this type of work. The levelling properties of many Class C dyes can be reasonably good in the absence of salt, and by the use of graphs the dyer can take advantage of this fact. The stage having been reached where no further exhaustion takes place in the absence of salt, the dye remaining in the bath can be exhausted on to the fibre by salt control. With this technique Class C dyes are in regular use in our dyehouse.

The graphs, therefore, apply to all classes of direct dyes, indicating the extent to which the dye will level itself and the amount of control necessary to achieve a satisfactory dyeing within an economical dyeing time. On the basis of this information the dyer can formulate his dyeing method. An example of this is given in the text (Fig. 5 and 6).

Mr. H. W. PARTRIDGE: What type of machine does the author consider most suitable for rayon cake dyeing?

Mr. FLANAGAN: The principles set out in this paper are applicable to any type of non-pressurised machine. Most of our work has been carried out on the Enka dyeing machine[5], in which the cakes are mounted vertically, but which is suitable for

dyeing only undried cakes. We have also considerable experience of the Longclose Coventry machine, which is designed to dye dried cakes too, and in which the cakes are mounted horizontally. Our experience of dyeing dried cakes, vertically mounted in the dyeing machine, is more limited, but from that limited experience we have found both types equally satisfactory.

Mr. PARTRIDGE: Does the tension of the samples on exhibition represent the optimum tension for dyeing?

Mr. FLANAGAN: The cake density and the traverse of the yarn are largely determined by spinning requirements and are not necessarily governed by the requirements of the dyer. For dyeing, a more permeable package—which could be achieved by increasing the yarn traverse speed —would be desirable, but this is limited by mechanical and other considerations.

Mr. J. BOSTON: Is the common salt dissolved before being added to the dyebath? If so, what method is recommended for controlling the addition of the salt to baths containing Class B dyes to give uniformity between different lots of the same shade? Also, at what rate does salting take place?

Mr. FLANAGAN: The salt is dissolved before being added to the dyebath, and the addition of the salt solution is regulated by a constant-flow device. The amount of salt required to produce an economical level of exhaustion of the dyebath and the rate of salt addition are determined by reference to the graphical data. For most Class B dyes the salt addition is made over a period of 2 hr.

Mr. A. S. FERN: Has the denier of the yarn used for the experimental work any effect on the final data shown in the graphs?

Mr. FLANAGAN: The experimental work has been carried out on the normal coarse-filament textile yarn. For fine-filament yarns the rate of dyeing will be a little greater, but for practical purposes the dyeing characteristics are very similar. This does not apply, of course, to high-tenacity viscose rayon yarns, where the fibre structure has been considerably modified by the method of spinning.

Mr. FERN: The graphs are based on the behaviour of single dyes under certain experimental conditions. When mixtures of dyes are used are the effects additive or is there any evidence of interference?

Mr. FLANAGAN: In general when using mixtures the effects are additive and predictable. However, the exhaustion control of a salt-sensitive dye used as a shading colour in a mixture may be lost because the other constituent dyes act as electrolyte. We have experienced also anomalous dyeing behaviour in certain mixtures, e.g. in the case of copper-containing dyes used in conjunction with dyes which have an avidity for copper. Anomalous behaviour of this type is not very common, and is usually detected in the laboratory when the suitability of dyes for use in mixtures is being examined.

Mr. H. R. HADFIELD: In one case, with a direct dye on viscose rayon, I found that in a series of levelling tests with various amounts of salt, as the exhaustion was decreased (by salt control) the levelling increased up to a point. Beyond this point the levelling was reduced. Has the lecturer observed this effect?

Mr. FLANAGAN: Presumably, in these levelling tests, dyed and undyed hanks were treated together in blank dyebaths which had been set with various concentrations of salt. As the salt concentration decreases the amount of dye desorbed from the dyed yarn increases, but whether or not this desorbed dye will be readsorbed by the undyed yarn will depend upon the affinity of the dye for the fibre, at the salt concentration of the dyebath. Since the levelling is estimated by comparing the difference in depth between the two hanks, it is quite possible that there could be an apparent decrease in levelling with decreasing salt concentration. The amount of dye retained in the bath is an important factor.

Mr. S. BURGESS: The S.D.C. Committee, in its Report on the Dyeing Properties of Direct Cotton Dyes [3], stated that the ABC classification had deliberately been made simple and general. The author implies in his paper that this means that it should not be extended to cover "special applications" such as the dyeing of viscose rayon cakes. He quotes the ICI classification of direct dyes to support his view. He will find that Durazol Orange 2G, a most useful dye from the standpoints of fastness and economics, is listed by ICI in Group 1, viz. "dyes which give perfect or nearly perfect results". Does he agree, and if so with what other dyes would he mix it to give e.g. fawns and greys on viscose rayon cakes?

Mr. FLANAGAN: The reasons for my preference for the graphical system to the S.D.C. classification have been given in an earlier reply (above).

With regard to Durazol Orange 2G, this is a very useful and economical dye, which is used extensively in viscose rayon cake dyeing. Provided that the rate of exhaustion with salt is carefully controlled, very level dyeings are obtained over a range of depths from écru to full golds. It can be used with Durazol Grey VG and Durazol Red 6B in the production of fast-to-light fawns and greys, although I prefer to base fawns on one of the homogeneous fast-to-light direct browns.

Some Experiments on the Condensation of Urea and Formaldehyde on Cellulosic Materials

J. ALVSAKER and H. A. TURNER

Experiments have been carried out in which the drying and high-temperature treatments of viscose rayon, impregnated with urea–formaldehyde precondensates, have taken place both in ventilated and in closed vessels. In this way the condensation has been effected with different concentrations of formaldehyde vapour in the surrounding air. These variations in the post-impregnation treatments affect the following quantities— proportion of resin fixed, fastness of the resin to removal by washing, crease resistance, stiffness, tensile strength, extension at break, and water retention. The relations between conditions of treatment and corresponding changes in the properties of the treated materials are discussed.

Introduction

Since the Standfast dyeing machine was introduced, and became a striking example of the successful use of baths consisting of molten, low-m.p. alloys as indifferent heat-exchanging media in the continuous treatment of fabrics, suggestions have been made that the device should be introduced into a variety of processing operations. In comparing the Standfast process for dyeing with the Williams hot-oil process or various pad–steam processes, it has been pointed out[1] that all have a common feature in that the heating medium for each is one into which the impregnate cannot readily diffuse, nor is there great risk of disturbing the distribution of padded solution. As a parallel device, molten-metal baths have been suggested for replacing the steamer in printing— either in complete substitution of the steam atmosphere or for locks at entry and delivery of a continuous pressure steamer[2]— and for dry heat treatments in finishing[3].

It is natural that molten-metal baths should be considered for giving the heat treatments necessary to complete the condensation of thermosetting resins applied as precondensates, or of formaldehyde with cellulose itself, in the various anti-crease or chemical anti-shrink finishes. Were an arrangement of this kind used in place of one of the more usual forms of baking stove, there would, of course, be new relations between the proportions of the heat reaching the cloth by radiation and by convection respectively, but large variations in this ratio exist already as between one design of baking stove and another. One feature which would distinguish the hot-metal method from stove methods is that, in the former, the cloth after impregnation, with or without drying, would be heated while closely surrounded with metal, i.e. in an unventilated space of small volume. Thus, presumably, the escape of formaldehyde, provided by uncombined reagent or evolved in one stage of the condensation, would be mechanically impeded, and the concentration of reagent in immediate contact with the fabric would be high. This could, in turn, lead to a different speed in the reactions of formaldehyde with other reagents or with cellulose, and could, in particular, affect the equilibrium position of any reversible reaction in which it took part.

Very many aspects of the reactions of formaldehyde which are exploited in the finishing of cellulosic textiles have been fully investigated, but there is less information generally available about the effect of external formaldehyde con-

centration than of other factors which influence the process. As molten-metal treatments are at a speculative stage, it was felt that a preliminary investigation of the effects of changing the external formaldehyde concentration should be made, under conditions in which the treatment was divorced from the specific presence of molten metal.

To this end an apparatus was constructed in which the essential component was a closed, glass-walled reaction vessel wound with a resistance wire so that it could be heated electrically to a desired temperature, and in which a suitably impregnated specimen could be suspended. The vessel could be maintained closed during the baking treatment, or a current of preheated air, into which formaldehyde vapour could be injected, could be passed through it at a desired speed and temperature (Fig. 4). The apparatus served for drying as well as baking. During the course of an experiment, samples of the air in the reaction vessel could be removed by means of a gas pipette attached thereto, and the formaldehyde content estimated by a colorimetric method.

Summary of Results

The number of variations possible in a simple experimental programme suggested by the foregoing proposals is very considerable, even when a standard viscose rayon fabric, a standard urea–formaldehyde precondensate, and a standard padding procedure are used. Thus a summary of the chief observations and conclusions must ignore a number of interesting incidental details.

EFFECTS OF VAPOUR CONCENTRATION OF FORMALDEHYDE

1. In experiments where heat treatments are given in a closed system (no air and vapour displacement) and where the formaldehyde is introduced (a) as uncondensed chemical on the impregnated fabric, (b) by injection of formaldehyde vapour during the treatment, or (c) by liberation from the urea–formaldehyde precondensate as a normal consequence of further condensation, its vapour pressure, and thus its effective concentration, appear to be diminished because of the deposition of solid polymers (polyoxymethylenes) in various parts of the system. The extent of this interference depends chiefly upon the temperature, being less as the temperature rises. There is evidence (Fig. 5), however, that formaldehyde is encouraged to change to the solid

form by liquid water included in the cellulosic fabric.

2. Increasing concentration of formaldehyde vapour in the surrounding atmosphere appears to retard the further condensation of hydroxymethylureas.

3. Especially with strong acid catalysts, increasing concentration of formaldehyde vapour leads to more extensive condensation of the reagent directly with cellulose to yield methylene derivatives. This diminishes the uptake and the retention of water rather than augmenting the resistance to creasing.

4. The effects of formaldehyde vapour concentration and the acidity of the catalyst are inter-related—

(a) If drying and baking are done in a moving air stream, leading to a low, constant, external concentration, increase in initial acidity leads to diminished resin fixation.

(b) In a closed system with high formaldehyde content, increasing acidity increases resin fixation.

(c) The increase in resin fixation on changing from a moving atmosphere to a stationary one is most marked for weakly acid catalysts.

CHANGES IN FABRIC PROPERTIES

1. Depression of the values for, respectively, moisture regain, water retention, and volume swelling in the treated specimens, before and after the resin is removed, may be used, in the normal way, as criteria for the extent of cross-linking in the cellulose. It is confirmed that these effects are generally greatest when the conditions favour direct methylenation of the cellulose but retard further condensation of the precondensate.

2. Changes in mechanical properties— resistance to creasing, stiffness, tensile strength, and extension at break— which owe their origin, at least in part, to internal resin formation, do not vary greatly over the range of drying and baking conditions employed when a weak acid is used as catalyst. The distinction is greater when results obtained with a weak acid catalyst are compared with those obtained with a strong one. Then— (a) for treatment in moving air (low, constant ambient formaldehyde concentration) little difference in crease-resistance and stiffness is observed, but tensile strength and extensibility are less with the strong acid; (b) for closed systems (concentration of formaldehyde vapour high and increasing) crease-resistance, tensile strength, and extensibility are lower with the stronger acid, and stiffness is higher.

Experimental

MATERIALS

Fabric

Spun viscose staple fibre; Utility 1005; yarn counts 32s × 32s cotton; ends/in. 88; picks/in. 60. All experimental samples were taken from a single piece of material, purified as follows: desized (2 hr. at 40°c. in 50 g. malt extract per litre), washed thoroughly in cold water, scoured (2 hr. at 90°c. in 5 g. textile flakes and 5 c.c. caustic soda

(53°Tw.) per litre), washed well, and dried at 45°c. without tension. Before use, samples taken from this stock were further treated in soap solution (0·05% in distilled water, 15 min. at 50°c.), washed in distilled water, and dried.

Formaldehyde

(A. Ashworth Ltd., Bury)

Formaldehyde content 40·05% (wt./vol.), 36·44% (wt./wt.); methanol 5·1%; free acid as formic 0·017%; sp.gr. 1·099; free from solid polymer and stored above 18°c. to prevent its formation.

Urea

(J. H. Towers Ltd., Widnes)

Pure crystals.

PREPARATION OF PRECONDENSATE

A lengthy investigation was made to decide how a standard precondensate should be prepared to bring condensation to the hydroxymethyl–bishydroxymethyl-urea stage cited in the patents of Tootal Broadhurst Lee Ltd.[4]. Urea (100 g.) was dissolved in 200 c.c. of formaldehyde solution which had first been neutralised with 1% caustic soda solution to pH 7·1 as measured with the glass electrode. This was followed by addition of 9·5 c.c. ammonium hydroxide (sp.gr. 0·88). The molar ratio of formaldehyde to urea was 1·60 : 1. The solution so prepared was divided into two portions, which were kept in a thermostat at the desired temperature, one at rest, one stirred. Determinations of viscosity were made from time to time at 20°c. in an Ostwald viscometer (B.S.S. Standard No. 2) with the necessary determination of specific gravity, pH, and concentration of uncombined formaldehyde (see below). Three preparations were made, at 25·2°, 20·2°, and 15·0°c. respectively. The preparation at 20·2°c. was also repeated with the formaldehyde solution adjusted initially to pH 8·5.

Unstirred	Stirred	pH	Temp. (°C.)
—○—	·—●—·	7·06	25·2
—△—	·—▲—·	7·04	20·2
—▽—	·—▼—·	8·54	20·2
—□—	·—■—·	7·40	15·0
—·—·—		Clear solution	
- - - -	- - - -	Turbidity with increasing formation of visible particles	
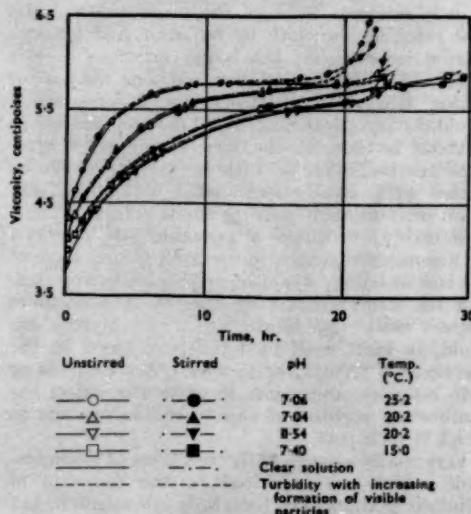
FIG. —Effects of Temperature and pH on the Condensation of Urea with Formaldehyde

Condensed at (°C.)	Neutralised to (pH)	
——○——	25·2	7·06
——△——	20·2	7·04
·——▲——·	20·2	7·04 Stirred
——×——	20·2	8·54
——□——	15·0	7·40
‑‑‑‑‑‑‑‑	Turbidity	
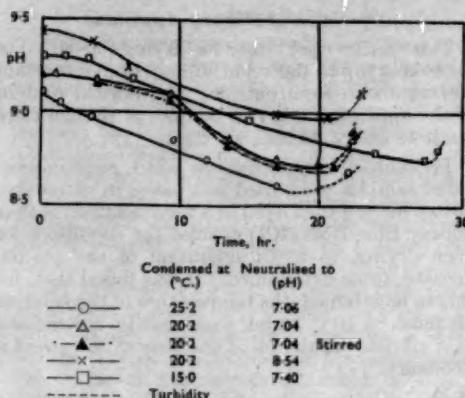
FIG. 2— Change of pH during Condensation in the Preparation of the Precondensate Solution
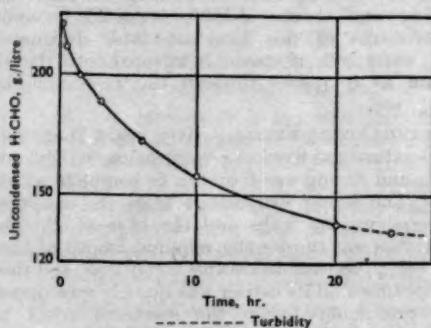
FIG. 3— Uncondensed Formaldehyde in the Condensation of Formaldehyde with Urea at 20·2°C.

The results (Fig. 1–3) may be summarised as follows—

(*a*) Stirring has little effect until the onset of turbidity

(*b*) As the temperature is made higher, the viscosity increases more rapidly, the onset of turbidity with its accompanying sharp increase in viscosity occurs earlier, and the fall in pH is more rapid after the reaction has commenced

(*c*) The higher the initial pH, the less rapid the precondensation and the slower the manifestation of all the associated effects

(*d*) The consumption of free formaldehyde has practically ceased (Fig. 3) before separation of solid condensate is seen.

It was decided, as a general practice, to make up the urea–formaldehyde solution as described above, allowing condensation to proceed at 20°c. until a viscosity of 5 centipoises had been reached (approx. 3½ hr.). The solution was then diluted with an equal volume of distilled water containing the selected catalyst and used at once for impregnation.

ACID CATALYSTS

The course of condensation was followed in detail, in the manner described above, with various kinds and proportions of catalyst. A reliable indication of the rate of condensation is given by the time required for the first sign of turbidity to appear (Table I).

TABLE I
Different Catalysts at 20·2°C.

Catalyst	Concn. (g./100 c.c.)	Initial pH	Time for Incipient Turbidity (hr.)
KH_2PO_4	1	6·5	65·5 (45·5*)
$NH_4H_2PO_4$	1	5·1	8·5
$NH_4H_2PO_4$	4	—	2·25
NH_4Cl	1	4·4	6·5

*At 25·2°c.

PADDING

Strips (approx. 36 in. × 8 in.) were cut weftwise from the prepared cloth. Each was soaked in the diluted precondensate, with catalyst added, for 5 min., and then padded through one nip (stainless steel–rubber) of a motor-driven laboratory pad
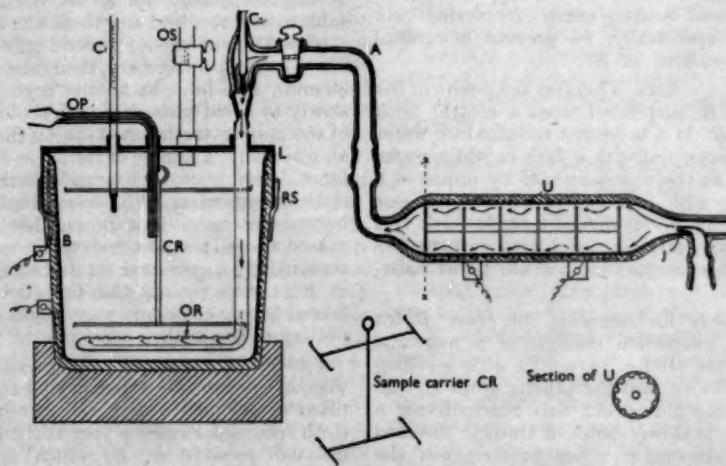
FIG. 4

mangle (F. Smith & Co. (Whitworth) Ltd.) with full weights on. Pick-ups were of the order of 100%, and were always calculated on the weight of cloth conditioned at 65% R.H. and room temperature.

HEAT TREATMENTS

Drying and baking were carried out in the apparatus sketched in Fig. 4. The main chamber B is a 4-litre Pyrex beaker resting in a wooden base. The walls of B are wound with 40 yd. of Nichrome wire (0·022 in. in diameter, 4·24 ohms per yard), which is then covered with a layer of asbestos. The beaker is closed with a brass cap L. The inner flat face of the cap is lined with a layer of rubber sheet cemented to the metal with urea–formaldehyde cement, and this rubber forms a seal with the edge of the beaker. The vessel is further sealed by a rubber sleeve RS passing over the side of B and the flange of L. Through holes in L are fixed a thermometer C_1, a capillary tube OP ending in a standard ground joint for connection to a sampling pipette, a glass tube OS with stopcock, connected to a vacuum pump, and a ring of glass tubing OR leading air, through perforations, into the base of B. Connection is made between OR and the preheater U by the glass joints of the adaptor A, which carries a second thermometer C_2 and a stopcock. U is a Pyrex glass tube wound with a resistance wire, insulated with a coating of asbestos, and fitted internally with a set of glass baffles. At the farther end of U is an inlet jet J for the introduction of water vapour, formaldehyde, etc., and a tube through which the main stream of air enters, having first passed through a Venturi flowmeter and then a heated, insulated vessel similar to B. The inclusion of this first stage of warming was found to be necessary to maintain the correct working temperature in B with the greatest speed of air flow.

The electric currents in the various windings were fed from the mains and regulated by means of variable transformers. The preheating stages are necessary when working in moving air (a) to obviate the total cooling effect of entering cold air, and (b), specifically, to prevent a vertical temperature gradient in B.

The padded specimen is held on the points of the wire carrier CR, suspended from a central hook in the cap of B. If it is desired to introduce water vapour, J is connected with a flask in which water can be boiled at the necessary rate by means of a heater mantle with Simmerstat control. At one stage formaldehyde vapour was introduced at this point from a generator in which zinc formate was heated, but the results were not altogether satisfactory.

The apparatus for sampling air from B for formaldehyde estimation consists of a mercury-filled gas-pipette (10 c.c. capacity) with levelling tube. Air is drawn into the pipette from B, and then, by turning a stopcock and manipulating a levelling tube, is slowly bubbled through distilled water in an absorption vessel to strip out the formaldehyde vapour.

Operation of Heating Apparatus

This can be used either for drying (60–80°c.) or for baking (up to 130°c.) in still air, or in a constant stream drawn from outside. The normal content of the apparatus was two samples of padded cloth (each 12 cm. × 14 cm.; wt. 2 g.).

Preliminary experiments in which resin-impregnated samples were dried and baked in currents of heated air and then dyed in a weak acidified bath of Solway Blue BNS (ICI) enabled the conditions for even drying, to avoid migration of the precondensate, to be determined. It was found that, for this to be attained, the temperature of the entering air must be 10°c. higher than that in B itself and that efficient insulation of the base of the vessel is necessary.

Drying

IN MOVING AIR— In general, drying was carried out for 1 hr. with air, at a specified temperature between 60°c. and 80°c., passing through the heating vessel at rates of 1000, 500, or 250 c.c./min. Experiments of this kind are later designated A_{500}, etc.; and, if steam is injected into the air stream as it passes through the preheater, by A_{500w}, etc.

IN THE CLOSED VESSEL— Here, again, the drying temperature was fixed at a value between 60°c. and 80°c., and drying was found to be complete within 1 hr. The liquid evaporated from the specimen collected on the walls and the base of B. The apparatus was run for the required length of time (see below) to establish stable conditions, and then the specimen on its carrier was quickly introduced. The precondensate on the specimen could be allowed to furnish all the formaldehyde vapour in B during the experiment (Method B), or this content could be enhanced as follows (Method C) (the procedure was worked out because the introduction of formaldehyde vapour from a generator was found to be difficult to control). A known weight of paraformaldehyde was placed on a watch-glass in B, which was then maintained at the drying temperature for 48 hr., during which time sublimation occurred and there was probably some condensation of vapour as solid polymer inside the lid. The temperature was then raised to 168°c. for 30 min., and brought to the drying temperature slowly to avoid undue formation of solid polymers of the polyoxymethylene type on the walls. When all was ready, a sample of the air in B was collected for a determination of formaldehyde content, the cloth specimen quickly introduced, and drying begun. Determinations showed that opening the lid caused a small temporary drop in the formaldehyde content which persisted for 1–2 min. only, so that in later experiments the first determination of formaldehyde content was made $2\frac{1}{2}$ min. after putting in the cloth.

Further independent determinations showed that, in experiments where drying and baking took place in a closed vessel, the introduction of the cloth specimen caused a very slight increase in the internal pressure in B, which never exceeded 20 mm. of water.

Baking

After the impregnated cloth had been dried, specimens were removed from the apparatus and at once placed in a stoppered glass container, in which they were left until the apparatus could be brought to the desired baking temperature. To allow stable conditions to be re-established, 1 hr. was fixed as a standard interval between the end of drying and the start of baking. Here, again, baking could be carried out in an air stream of known velocity (A_{500}, A_{500w}), in a closed vessel without formaldehyde enrichment (B) or in a closed vessel with added formaldehyde (C). The temperature was fixed at 130°c., the time at 5 min. With suitable manipulation of the various heating currents the fall of about 5°c. in temperature when the specimen was introduced could be reversed within 1 min. (Methods B and C) to 1½ min. (Method A). After baking, cloth specimens were exposed to air for 10 min., treated for 5 min. at 50°c. in a solution containing 0·1% soap and 0·1% sodium carbonate, washed in hot and then in cold distilled water, and dried at 30°c.

ESTIMATION OF FORMALDEHYDE

(1) In Precondensates, etc.

A 20-c.c. portion of a reaction mixture was diluted to 500 c.c. An aliquot (25 c.c.) of the diluted solution was added to 40 c.c. of 0·1 N. iodine together with 8 c.c. of 2 N. sodium hydroxide, allowed to stand for 15 min., acidified with 9 c.c. of 2 N. sulphuric acid, and back-titrated with standard 0·1055 N. sodium thiosulphate solution.

(2) Formaldehyde Vapour in Air Samples

Samples of air were removed from B by means of the gas-pipette already described. To ensure removal of a representative sample, the air was removed and re-introduced into B three times before being taken for estimation. After levelling off to atmospheric pressure and reading the temperature, the air (10 c.c.) was bubbled slowly through water (7·5 c.c.) in the absorber. If necessary, further volumes of air could be abstracted from B and passed through the absorber. In a trial in which the air was passed from the regular absorber through a second, connected in series, it was found that 120 c.c. of air could be passed with a loss of only 1% of the total formaldehyde in the first absorber. Very much smaller volumes than this were normally used for sampling.

After running out the extract, the absorber was washed with several changes of distilled water, and the whole was collected and made up to volume. In carrying out baking experiments, it was found necessary to sacrifice a certain amount of accuracy by continuing sampling after the cloth specimen had been removed, since 5 min. was too short a time to allow the necessary volume of air to be removed. This applied only to experiments A. For B or C experiments the concentration of formaldehyde in the abstracted air was great enough to allow an estimation with one 10-c.c. sample. This was generally removed 1 min. before the baking period terminated.

Colorimetric determination of formaldehyde in the extracts was made by a modification of the method of Walker[5]. Purified Acid Fuchsine (1 g.) was dissolved in 600 c.c. hot water, which was then cooled, 8·5 g. sodium metabisulphite was added, followed by 10 c.c. concentrated hydrochloric acid, and the whole diluted to 1 litre. The reagent was stored in completely filled, closely stoppered amber glass bottles (claimed to keep thus for up to 2 years). The sensitivity of any Schiff's reagent depends upon reducing the excess of sulphurous acid to the smallest possible value. In this case, a series of preparations was made in which the proportion of metabisulphite varied from one to another. To each was added the same volume of standard formaldehyde solution, and the ensuing colour was measured on the Spekker absorptiometer. The preparation developing the most intense colour was chosen as the pattern for all further determinations.

The reagent prepared as described contained a very slight excess of Fuchsine, and was slightly pink in acid solution. It also changed colour slightly on change of temperature, and stock reagent taken from the refrigerator was allowed to stand overnight at laboratory temperature before the bottle was opened for use. Calibration was carried out by refluxing paraform in distilled water, estimating the formaldehyde content of the extract iodometrically, and preparing a series of standard solutions by dilution of this extract.

In an estimation, 1·5 c.c. of concentrated sulphuric acid was added to 7·5 c.c. of the formaldehyde solution in a stoppered flask (25 c.c.). After cooling to room temperature, 7·5 c.c. of Schiff's reagent was added, and the flask closed and allowed to stand for 3 hr. in the dark (the colour deepens for 3 hr. and then slowly fades). The optical density was then measured on the Spekker absorptiometer. By this procedure a strictly linear calibration curve relating formaldehyde content with Spekker readings was obtained for quantities ranging between 3×10^{-6} and $1·5 \times 10^{-4}$ moles of formaldehyde.

The concentration of formaldehyde in the air within B during a drying or baking experiment was calculated from the results of the estimation in terms of milligrams per 1000 c.c. at the temperature of the operation, and thence in the form of partial pressure of formaldehyde in millimetres of mercury.

ANALYTICAL DETERMINATIONS ON TREATED CLOTH SAMPLES

Polymerised but Uncondensed Formaldehyde[6]

After drying, one of the two specimens was cut in two, and one piece put to soak in 100 c.c. of distilled water. The other was baked along with the intact specimen, and then put similarly to soak. After standing overnight* each solution was neutralised with 0·1 N. sodium hydroxide using thymolphthalein as indicator; 50 c.c. of 0·1 N. sodium sulphite was neutralised with 0·1 N. hydrochloric acid, also to thymolphthalein, and then

* *Caution*— The flasks used for these determinations must first stand with water containing indicator to enable any which may develop alkalinity to be rejected.

B2

added to the extract.   The reaction proceeds thus—

$$H \cdot CHO + Na_2SO_3 + H_2O = H \cdot CH(OH) \cdot SO_3Na + NaOH$$

The alkali liberated after 30 min. was titrated with standard 0·1 N. hydrochloric acid, and the formaldehyde content calculated as a percentage on the weight of the dry extracted specimen. The cloth specimens were washed well, dried, and reserved for estimations of resin content.

A control experiment in which hydroxymethyl-urea was prepared and boiled in water for several hours showed no development of alkalinity, indicating the presence of free formaldehyde, when sodium sulphite was added to the cold solution. Formaldehyde estimated in a cold aqueous extract of the sample is therefore unlikely to have been combined with urea at any stage of the polycondensation.

Some estimations on portions of the same padded cloth, dried and baked in different ways, are given in Table II. The very large discrepancy in the formaldehyde-vapour content of the air in the heating chamber as determined by procedures (a) and (b) has so far received no satisfactory explanation. In the B and C methods there is a considerable weight of formaldehyde lost apparently from a closed vessel. Tentatively the suggestion is made that attempts to insulate the heating vessel uniformly had not been successful, and that there were "cold spots" in which polyoxy-methylenes depolymerised from deposits on the cloth could re-form. This, if true, would have a considerable bearing on the design of large-scale polymerisers, since aldehyde vaporised from the cloth primarily by radiation heating might find cool places on the casing at which it could deposit. Alternatively, the formaldehyde may be present in the liquid which condenses in the cold vessel during drying.

Formaldehyde was further detected, combined as hexamethylene-tetramine, on the dried specimens, and also on those which had been dried and baked, by the mercuric chloride method. More was detected on dried than on dried-and-baked, but the difference was never very great, and neither this nor other methods tried gave reliable quantitative results.

Estimation of Resin Content

(i) MOISTURE CONTENT— The specimen was conditioned for 10 days over saturated ammonium nitrite solution (65% R.H. at 20°C.) and weighed. It was dried for 90 min. at 115°C. in an oven with air circulation, cooled over phosphorus pentoxide for 2½ hr., and again weighed. The moisture content was calculated on the dry weight of the specimen (calculated dry weight = W_D).

(ii) RESIN CONTENT— A rectangular pattern (11 cm. × 8 cm., weight ca. 1·5 g.) was frayed along the cut edges for a few threads in order to prevent loss of material, conditioned along with the specimen for moisture estimation, and weighed. It was then treated in the Marney machine with a solution of soap and sodium carbonate (2·5 g. of each per litre) for 5 min. at 90°C. and a liquor ratio of 40 : 1, washed in hot and cold distilled water, dried at 45°C. and then at 115°C. for 70 min., cooled over phosphorus pentoxide for 50 min., and weighed (soap-extracted weight = W_S). The same specimen was now extracted with acid (0·1 N. hydrochloric acid for 60 min. at 60°C., liquor ratio as in Marney machine), washed, and dried as before (acid-extracted weight = W_A).

(iii) REMOVABLE RESIN—

$$R_r = \frac{W_D - W_S}{W_A} \times 100\%$$

(iv) TOTAL RESIN—

$$R_t = \frac{W_D - W_A}{W_A} \times 100\%$$

(v) SOLUBLE RESIN—

$$R_s = \frac{R_r}{R_t} \cdot 100$$

i.e. R_r expressed as a fraction of the total resin and not of the sample.

(vi) For some purposes it is convenient to refer the resin content to a cloth in which the "expression" (take-up) has reached the uniform figure of 100%. The two most useful figures are—

$$E_t = \frac{R_t}{\text{Take-up}} \times 100 \quad \text{and} \quad E_i = \frac{R_t - R_r}{\text{Take-up}} \times 100$$

The latter value is the standard content of wash-resistant resin.

• TABLE II

(Catalyst 1% KH_2PO_4)

Take-up (%)	Drying (60 min.) Method	Temp. (°C.)	Baking (5 min.) Method	Temp. (°C.)	Uncombined H·CHO After Drying (%)	After Baking (%)	Increase in H·CHO Vapour in B (a)*	(b)*	(a)—(b)
99·5	A₁₀₀₀	60	A₁₀₀₀	130	1·89	0·81	10·8	—	—
95·1	B	60	B	130	1·25	0·37	8·8	0·65	8·15
93·7	C	60	C	130	1·84	0·81	10·3	2·40	7·9
95·2	A₁₀₀₀	80	A₁₀₀₀	130	0·82	0·13	6·9	—	—
97·7	B	80	B	130	0·58	0·31	2·7	0·6	2·1
93·7	C	80	C	130	0·87	0·33	5·4	2·0	3·4

*(a) = Increase in concentration of formaldehyde vapour in air of heating chamber (mg./1000 c.c.), calculated on the assumption that the difference between the uncondensed formaldehyde contents in the sample after drying and after baking respectively is volatilised into air at 130°C.

(b) = Corresponding value determined by direct analysis of air samples.

TABLE III

(Catalyst 1% KH_2PO_4. Drying temp. 60°c.)

Sample	Method of Drying and Baking	Take-up (%)	Moisture (%)	Resin Contents (%)				
				R_r	R_4	R_3	E_4	E_1
0*	None	—	16·34	0·21	0·79	—	—	—
1*	A_{1000}	87·2	15·97	0·24	0·76	—	—	—
2	A_{1000}	93·3	14·56	4·99	13·76	36·5	14·7	9·3
3	A_{1000}	94·0	14·87	5·91	14·64	40·4	15·6	9·3
4	A_{1000w}	91·4	14·99	4·52	12·43	36·4	13·6	8·7
5	A_{500}	95·4	14·86	5·96	13·19	39·3	15·9	9·7
6	A_{250}	98·1	13·97	6·22	16·64	37·4	16·9	10·6
7	A_{250}	92·5	14·74	5·36	14·53	36·9	15·7	9·9
8	B	95·5	13·64	6·49	19·10	34·0	20·0	13·2
9	B	94·1	13·93	5·91	19·93	29·7	21·2	14·9
10	C	94·4	13·70	6·98	18·65	37·4	18·9	12·4
11	C	93·9	13·90	5·65	18·36	30·8	19·6	13·4
12*	C	87·6	16·16	0·43	0·74	—	—	—
13*	C	82·3	16·27	1·34	1·76	—	—	—

*Samples 0, 1, 12, and 13 are controls. Sample 0 received no treatment at all before being submitted to a "drying" and "baking" treatment. Samples 1 and 12 were padded through plain water only; 13 was padded through water containing the dissolved catalyst.

The chief results of these determinations will be given later in Fig. 9–11, but a representative series of values is quoted in Table III.

Moisture Regain[7]

Specimens (of weight approx. 0·5 g.) were dried in tared weighing bottles over phosphorus pentoxide for 5 weeks to constant weight. Each bottle was then transferred to one of a series of desiccators, each containing a saturated solution of an appropriate salt to establish a fixed relative humidity in the air above it. The separate humidities ranged in value from 20% at 20°c. (potassium acetate) to 90% at 20°c. (sodium sulphate). The specimen was retained in the appropriate desiccator for periods up to 5 weeks until constant weight had been attained. The result was expressed either in terms of increase in weight calculated upon the dry weight of cellulose plus accompanying resin or on the dry weight of the cellulose alone.

Water Retention and Volume Swelling

To supplement the information given by moisture uptake values concerning the degrees of cross-linking and methylenation on the cellulose, and their probable direct effects upon shrinkage during wetting or upon resistance to creasing, measurements of water retention were made by the method of Preston, Nimkar, and Gundavda[7, 8]. The apparatus is a cylindrical pot of finely porous unglazed porcelain, closed with a rubber bung through which a glass tube passes and then leads to a suitable water-trap, a connection to a manometer, and a connection to a vacuum pump. The base of the pot and small strips of the side at the ends are coated with paraffin wax. The cloth in the form of a long strip, wide enough if possible to cover the uncoated surface of the porcelain, is soaked in water for 2 hr., wrapped in a single layer round the pot, and covered with a layer of polythene sheet. The pot itself is filled completely with water. If a vacuum is applied to the apparatus,

it causes a corresponding diminution in the local vapour pressure of water within the capillaries in the porcelain, and water will be removed from the surrounding cloth until the vapour pressure of water in the cloth is reduced to that in the capillaries. Free water is thus removed from all except the finest pores in the cloth, from which any form of mechanical extraction would fail to remove it. The method gives results comparable with those obtained with a high-speed centrifuge but more quickly. The end of the removal is shown by water ceasing to flow from the porous pot into the trap.

The operating vacuum was 36 cm. of mercury and the time required for water removal was 8 min. The specimens were placed in a dry tared weighing bottle, weighed, and dried to constant weight at 115°c. From the water retention $W\%$ the equivalent volume swelling is given by—

$$(W - 20) \times 1·52$$

The figure 20 is the correction for capillary water and free space, and 1·52 is the specific gravity of viscose rayon. The swelling ratio is the ratio between the volumes in the swollen and the unswollen states.

Estimation of Nitrogen

As discussed later, the main interest lies in the residual nitrogen content after extraction of treated cloths with acid. The proportion of nitrogen was therefore very small, and a micro-Kjeldahl method was adopted, for the details of which we are indebted to Dr. M. Horwood of Messrs. Norman Evans & Rais Ltd.

REAGENTS— A— Concentrated sulphuric acid (B.D.H. Microanalytical Reagent)

B— Catalyst, 32 g. potassium sulphate + 5 g. mercuric sulphate + 1 g. powdered selenium (all AnalaR)

C— Sodium hydroxide (400 g./litre)

D— Ammonium nickel sulphate (0·1 M.)

E— Hydrochloric acid (0·015 N., equivalent to 0·21 mg. nitrogen per c.c.)

F— Methyl Red (1 g. per litre of 96% ethanol)

G— Methylene Blue (as Methyl Red).

DIGESTION— The specimen (0·5 g.), 2 g. of *B*, and 4 c.c. of *A* were heated in the usual digestion flask to a gentle boil, maintained thereat until 15 min. after the solution had become clear, cooled, diluted to 25 c.c., and transferred to the usual pattern of micro-distillation apparatus (Quickfit & Quartz), which had first been well steamed, chiefly to remove any alkali from the glass. Free alkali was tested for by distilling over two-thirds of a liquor containing 1 c.c. of *C* in 30 c.c. of water. The distillate should not show as alkaline on adding 1 drop of *E* and 1 drop of *F*. Transfer of the digestion mixture was followed by three separate washings (5 c.c. of distilled water each) and, finally, addition of 20 c.c. of *C*. The whole was steam-distilled into 10 c.c. of *D* with the condenser tube dipping below the surface until 100 c.c. of distillate had been collected in 20 min. The distillate was titrated with *E* after adding 5 drops of *F* as indicator and 2 drops of *G* as internal filter. The end-point was indicated by a grey colour intermediate between green and violet. It was found unnecessary to tablet the cut specimens of cloth before digestion.

Swelling of Fibres in Cuprammonium Hydroxide

As a qualitative test of efficiency of chemical cross-linking, the rate of solution of resin-treated samples in cuprammonium hydroxide (15 g. copper plus 200 g. ammonia (NH₃) per litre) was determined after they had been acid-extracted. The time of complete solution (which was under 1 hr. for plain viscose rayon) extended from 1 hr. to more than 96 hr. Some information was also obtained by embedding threads from specimens in paraffin wax, cutting cross-sections, clearing and mounting in ethanol, and then displacing this with cuprammonium reagent. Observation under the microscope enabled the whole sequence of swelling and solution to be observed.

PHYSICAL PROPERTIES

Crease Resistance

The B.C.I.R.A. (British Cotton Industry Research Association) instrument was used, and since the amount of cloth from each experiment was limited, a test-piece (warp 2 cm., weft 5 cm.) smaller than the recommended one had to be used. The test was carried out on cloth fully conditioned at 65% R.H. and 20°C. Creasing was under a total load of 2 kg. for 1 min., and the angle of recovery was measured 30 sec. after the weight had been removed. The modulus of crease recovery is expressed as—

$$\frac{\text{Measured angle} \times 100}{180}$$

Bending Length

This was measured on the same instrument, the standard bending length being calculated by the method of Peirce[9]. Only one test-piece of standard dimensions could be cut from each treated specimen, but control experiments with larger specimens showed that satisfactory agreement could be expected between the results with different pieces from the same specimens.

Breaking Strength and Extensibility

These properties were measured by tests on dissected weft threads, 10 per specimen, 88 mm. between jaws, in a Goodbrand single-thread tester.

Experimental Results

CONCENTRATION OF FORMALDEHYDE VAPOUR DURING DRYING

The partial pressure of formaldehyde vapour in the heating vessel *B* (Fig. 4) for a series of experiments in which drying was carried out by different methods is shown in Fig. 5 and 6, of which Fig. 5 is restricted to drying at 60°C. and Fig. 6 shows the effect of changing the temperature from 60° to 80°C. The catalyst was 1% potassium dihydrogen phosphate throughout the series. The general

Method	Take-up (%)
A₁₀₀₀	—
A₅₀₀	—
A₂₅₀	—
B	94·1
B	95·6
C	93·9
C	94·8
C	(Padded in water alone)
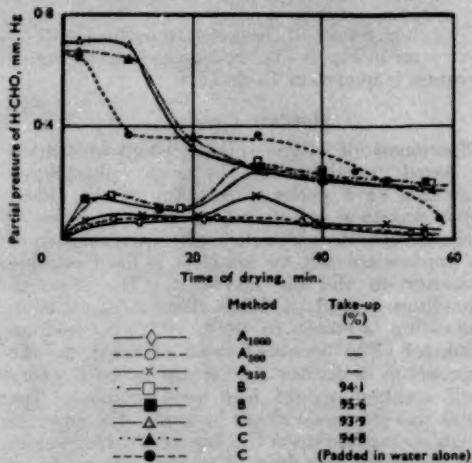
FIG. 5— Effect of Drying Conditions at 60°C. on the Partial Pressure of Formaldehyde

Method	Temp. (°C.)
A₁₀₀₀	60
B	60
C	60
A₁₀₀₀	80
B	80
C	80
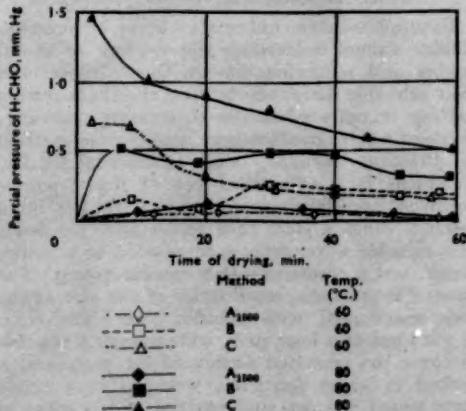
FIG. 6— Effect of Temperature of Drying on the Partial Pressure of Formaldehyde

trend of the results is what might reasonably be predicted—

1. Drying of impregnated cloth in a moving air stream (Method A) leads to a low partial pressure of formaldehyde. Since the formaldehyde in the vessel has to be obtained from the cloth, the pressure is initially almost zero; it rises to a steady value which persists for some 30 min., and then diminishes as the cloth becomes exhausted.

2. The slower the air current the higher the maximum accumulation of vapour; but, except around this maximum, an air current of 250 c.c. per min. is still sufficient to remove aldehyde vapour as it is liberated.

3. Drying in an unventilated vessel (Methods B and C) leads to much higher aldehyde concentrations when steady conditions are reached, and there are indications that there is a solid formaldehyde phase, formed in some part of the vessel, in equilibrium with a constant vapour concentration. The partial pressure rises to this value when there has been no initial enrichment of the system (i.e. in Method B, where, presumably, formaldehyde on the cloth which has reacted neither with urea nor with the cellulose itself first vaporises), or falls to it when initial enrichment has taken place (in Method C).

4. Raising the drying temperature from 60° to 80°c. does not alter essentially the general behaviour, but, in the non-ventilated systems, leads to high vapour pressures of formaldehyde.

5. In all non-ventilated systems, the gradual fall of vapour pressure of formaldehyde with time suggests that some of it is again polymerising.

CONCENTRATION OF FORMALDEHYDE VAPOUR DURING BAKING

As explained earlier, a period has to elapse between drying and baking, while the heating vessel is raised to its new temperature. During this time the dried specimen is preserved apart.
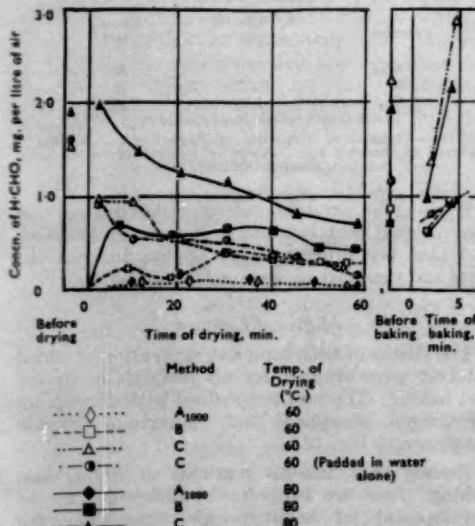
FIG. 7— Concentration of Formaldehyde Vapour during Drying and Baking

Fig. 7 shows graphically the vapour pressure relations when drying is followed by baking, the state of the atmosphere in the baking vessel before introduction of the impregnated cloth being shown by the points on the separating ordinate. The data for the baking experiments only are given on a larger scale in Fig. 8.
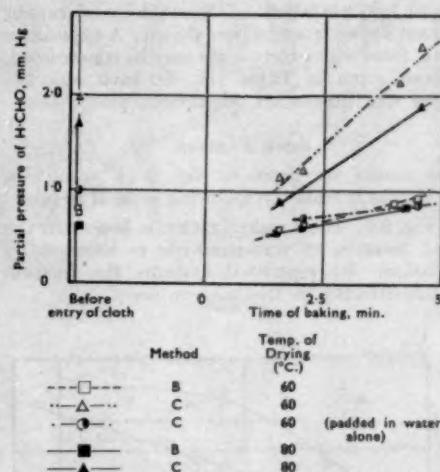
FIG. 8— Effect of Drying and Baking Conditions on the Partial Pressure of Formaldehyde during Baking

As explained previously, sampling in the ventilated experiments A_{1000} takes so long that the vapour pressure at the end of the experiment alone could be given. It is very much smaller than the values set up during the course of the unventilated experiments. It is therefore inconvenient to show on the curves, but is given in Table IV.

TABLE IV

Method of Drying and Baking	Temp. of Drying (°c.)	Partial Pressure of H·CHO at End of Baking (mm. Hg)
A_{1000}	60	0·020
A_{1000w}	60	0·017
A_{1000}	80	0·017
A_{500}	60	0·085
A_{250}	60	0·37

It will be seen that, within the closed chamber (Methods B and C), these values can be exceeded many times, especially in an enriched atmosphere. The results for Methods A, B, and C may therefore cover a wide range of concentrations of formaldehyde vapour around a cloth during baking. The lower values (in ventilated systems) may correspond to present-day conditions in some of the most thoroughly ventilated stoves; the higher might represent conditions in a molten-metal polymeriser after a long run.

That, even in a closed enriched system, the entering cloth contributes to the formaldehyde content is shown by comparison of the curve marked △ and that marked ⊙ in Fig. 8. The latter represents the entry of a cloth padded in

water alone, dried, and "baked" in an enriched atmosphere. It will be seen that increase in the formaldehyde vapour content of the air is much less than when a cloth containing precondensate is introduced.

RESIN CONTENT

The effect of various factors, including the external concentration of formaldehyde vapour discussed above, may be now shown. A typical set of data, from which the curves may be constructed, has been given in Table III. In each case the catalyst was potassium dihydrogen phosphate.

Resin Fixation

The results are given in Fig. 9–11. Study of these figures reveals the following general trends—

1 (Fig. 9). Total resin fixation is less when the partial pressure of formaldehyde is lessened by ventilation. In ventilated systems the fixation increases steadily as the take-up rises.

FIG. 10— Variation of Proportion of Resin fast to Soaping ($R_t - R_r$ and removed by Soaping (R_r), with Take-up of Original Precondensate Solution

FIG. 9— Effect of Take-up of Precondensate Solution during padding upon Total Resin Fixation R_t

6. The conclusions reached above are subject to some qualification when the proportions of the two kinds of resin are corrected to values which would be obtained for a standard take-up of 100%. Then it is seen (Fig. 11) that the differentiation
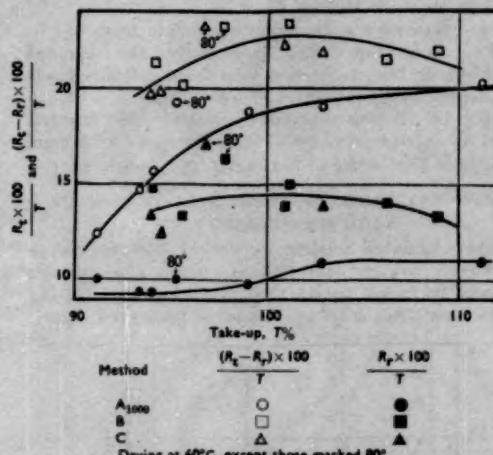
FIG. 11— Variation of Proportion of Resin fast to, and that removed by, Soaping with Take-up of Original Precondensate Solution. Corrected to 100% take-up

2. The extent of resin fixation may be affected also by migration of the precondensate to the surface during drying. Ventilated drying is likely to encourage this migration.

3 (Fig. 9). Corresponding values are higher in non-ventilated than in ventilated atmospheres, but there is a similar relation between fixation and liquor take-up. Preliminary enrichment of the working atmosphere with formaldehyde vapour seems to have little effect.

4. Increased drying temperature, under the conditions employed here, leads to increased total fixation.

5 (Fig. 10). Within the total of fixed resin it is the portion that is fast to soaping which is most affected by the conditions of drying and baking: the portion removed by soap is pretty much the same, for a given take-up, whether ventilated or unventilated conditions are used.

between the results of ventilated and of unventilated heat treatments is more pronounced, and that the differentiation applies to both the total and the "fast-to-washing" resin contents.

Effect of Catalyst

The effects of both kind and proportion of added catalyst were studied for all methods of drying and baking. The results obtained with ammonium dihydrogen phosphate and ammonium chloride are shown in Fig. 12.

Among the different methods of drying and baking, there are likely to be differences in the development of acidity with time. For the phosphate, at least, ventilation might be expected to have two opposing effects, removing water most

rapidly of all three methods and therefore tending to discourage hydrolysis, but at the same time

regain as the resin content rises. The results represented by the top two curves were obtained
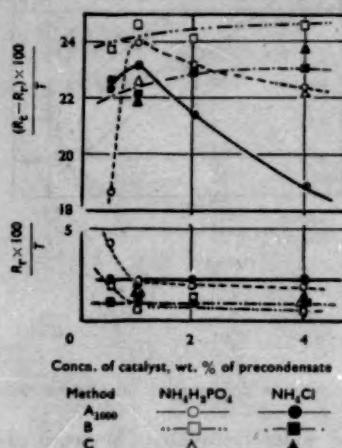
FIG. 12— Relation between Fixation and Concentration of Catalyst

FIG. 13— Moisture Absorption Isotherms at 20°c.

removing ammonia most completely as it is liberated, and therefore tending to increase hydrolysis.

The observed results do, in fact, show a very chraacteristic difference between ventilated and unventilated treatments; Fig. 12 shows the separation into removable and non-removable resin. In ventilated systems there is a pronounced maximum value of resin fixation with increasing catalyst concentration; whereas in unventilated systems the effect of concentration is small, and, further, the fact of previous enrichment seems to have very little significance. The presence of a maximum in ventilated systems may be explained as follows. Ventilation accelerates the full development of acid from the ammonium salt. After a certain concentration of free acid has been exceeded, the depolymerising effect on the condensate already formed becomes more pronounced.

MOISTURE REGAIN

When attempting to determine the relation between moisture regain and the changes coming from reactions accompanying resin condensation, the effects of heat treatment alone upon the cellulose must be considered. For this reason, cloth samples which had been padded in water only were passed through the typical drying and baking stages of ventilated and unventilated heat treatments, and moisture isotherms at 20°c. determined with them also.

Fig. 13 shows that, even compared with heated unimpregnated cloth, the presence of resin further depresses the moisture uptake, but that the influence of the conditions under which drying and baking have taken place is not very important. Having established this fact, we see from Fig. 14 that there is a steady diminution of moisture
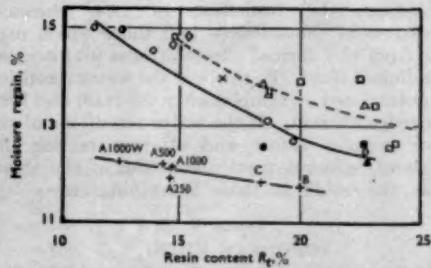
FIG. 14—Effect of Temperature of Drying and of Methods of Drying and Baking on the Moisture Regain at 65% R.H. and 20°c.
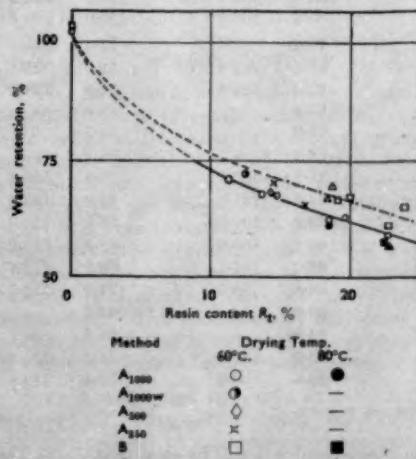
FIG. 15— Effect of Resin Content on Water Retention (Catalyst 1% KH$_2$PO$_4$)

by conditioning after a short stove drying and are seen to be erratic, the general tendency being for the moisture regain to be lower with specimens that have been heat-treated in moving air. When there has been prolonged and exhaustive drying at room temperature over phosphorus pentoxide, there is a linear relation between regain and resin content which is independent of the method of processing.

All the experiments were performed with 1% potassium dihydrogen phosphate as catalyst.

WATER RETENTION

The effects of resin content on the water retention and on the derived volume swelling are indicated in Fig. 15 and 16 respectively. It is seen that, while there is some scatter in the results, drying and baking in moving air does seem to have resulted in a greater blocking of water-attracting groups and a greater degree of cross-linking for the same total fixation of resin than do treatments in unventilated atmospheres. This is largely a reflection of the greater efficiency of water removal.

In considering these effects, a distinction must be made, as already noted, between those which arise from the formation of new chemical derivatives of the cellulose and those which may come from the normal effects of heat and acid on the cellulose itself. To this end the water retention was determined on samples after the resin had been removed with acid. If the water retentions of the above samples before and after extraction are compared, without particularisation of the treatments, the results in Table V are obtained.

TABLE V
(Catalyst 1% KH₂PO₄)

Total Resin Content R_t (%)	Water Retention (%)		Volume Swelling (%)	
	Before Acid Extraction	After Acid Extraction	Before Acid Extraction	After Acid Extraction
—*	106·6	99·5	131·6	120·9
—*	107·2	101·3	132·0	123·4
—*	100·6	102·4	122·4	125·2
—*	105·6	102·7	130·0	125·8
11·3	70·6	—	77·4	—
13·7	67·4	102·3	72·0	125·1
14·6	67·3	104·5	71·9	128·0
18·5	61·8	—	63·5	—
19·6	62·6	—	64·7	—
22·7	58·8	—	58·9	—
12·4	71·9	105·7	78·8	130·1
14·2	68·0	101·2	72·9	123·4
14·5	70·0	102·3	75·9	125·0
16·6	65·1	100·9	68·5	123·0
19·1	66·0	101·1	69·9	123·2
19·9	66·8	99·9	71·2	121·5
22·7	60·9	—	62·2	—
23·0	64·9	—	68·2	—
18·4	66·9	100·2	71·2	121·8
18·7	69·6	98·8	75·4	119·8

* Padded only in water

From these results it will be seen that— (a) The acid extraction treatment lowers the water retention in the absence of original resin. (b) Most of the
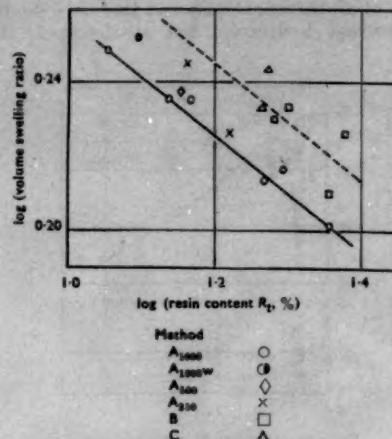
FIG. 16— Effect of Resin Content upon Volume Swelling

diminished water retention in presence of resin arises from the direct intervention of the condensation itself; differences are largely due to differences in the proportion or conditions of formation of the resin; and removal of the condensate by acid extraction practically restores the retention properties of the original cloth.

To see whether the use of more strongly acid catalysts would cause a departure from the very small modification caused by potassium dihydrogen phosphate, ammonium phosphate and ammonium chloride were used instead. It is difficult to display all the observations graphically, and they are given in Table VI.

Here, by comparison with Table V, it is shown that— (a) The stronger the acid catalyst, the less the water retention, although the effect of increasing acidity is not very large. (b) The more strongly acid the catalyst, the greater the modification of the underlying cellulose as reflected by the diminished water retention of the pattern after removing the resin with acid. For a given concentration of a specified catalyst, the least diminution in the water retention is caused by drying and baking in moving air, and the greatest is obtained with enrichment of formaldehyde in a closed chamber. Where water is injected during the heat treatments (A_{1000w}) the drop in water retention is very much less.

FORMALDEHYDE IN EXTRACTED SPECIMENS

It has been implied that the somewhat lower values found for water retention in the viscose rayon fabric, after resin has been condensed upon it and then removed with acid, might be due to the modifying effects of acid and high temperature on the original fabric. It is possible, however, that some combination of formaldehyde and cellulose, e.g. methylene ethers, might persist, even after the acid extraction. More drastic means were used to decompose any compound of this kind by boiling for 30 min. in 2 N. sulphuric acid containing 10 g. sodium sulphate (Na₂SO₄) per litre and then

TABLE VI

Method of Drying and Baking	Catalyst (%)	R_t	Analysis of Acid-extracted Specimens			Water Retention (%) Before After Acid Extraction		Volume Swelling (%) Before After Acid Extraction	
			H·CHO (%)	N (%)	Molar Ratio $\dfrac{CH_2O}{CO(NH_2)_2}$	Before	After	Before	After
			$NH_4H_2PO_4$ (dried at 60°c., baked at 130°c.)						
A_{1000}	0·5	23·1	0·104	0·066	1·46	60·2	98·7	61·1	119·7
	1·0	26·2	—	—	—	63·4	98·5	66·0	119·3
	2·0	25·1	—	—	—	55·4	100·0	53·8	121·5
	4·0	24·5	—	—	—	60·5	102·1	61·5	124·9
B	0·5	24·5	0·195	0·096	1·89	65·2	97·4	68·7	117·8
	1·0	24·8	0·288	0·164	1·64	65·4	98·1	69·0	118·7
	2·0	26·2	0·706	0·362	1·82	54·8	98·9	52·9	119·9
	4·0	26·1	0·465	0·225	1·93	59·3	96·0	59·7	115·4
C	1·0	24·6	0·413	0·231	1·66	55·2	94·1	53·3	112·4
	4·0	24·4	0·242	0·112	2·02	54·2	93·0	51·8	110·9
			NH_4Cl (dried at 60°c., baked at 130°c.)						
A_{1000}	0·5	24·3	0·445	0·214	1·94	64·0	94·4	66·9	113·0
	1·0	24·8	—	—	—	62·1	94·7	63·9	113·0
	2·0	23·3	—	—	—	64·4	90·7	67·4	107·3
	4·0	20·8	0·031	0·014	2·07	64·6	93·7	67·8	111·6
A_{1000w}	4·0	22·1	—	—	—	85·8	89·0	100·0	104·9
B	0·5	23·9	—	—	—	61·7	90·6	63·4	107·2
	1·0	23·8	0·914	0·446	2·08	59·7	85·8	60·3	100·0
	2·0	24·1	—	—	—	53·1	81·2	50·3	93·0
	4·0	24·5	0·439	0·134	3·06	50·8	78·9	46·8	89·0
C	1·0	22·2	0·797	0·328	2·26	55·2	84·0	53·5	97·2
	4·0	22·2	0·230	0·068	3·15	50·2	76·2	45·6	85·4

TABLE VII

Catalyst	Method of Drying and Baking	H·CHO on Extracted Specimens (%) Before After Difference Ammonia Treatment (%)			Water Retention (%)
		Before Ammonia	After Treatment	Difference (%)	
0·5% $NH_4H_2PO_4$	A_{1000}	0·104	0·099	4·8	98·7
	B	0·195	0·190	2·4	97·4
2·0% NH_4Cl	A_{1000}	0·036	0·033	9·1	90·7
	B	0·609	0·588	3·5	81·2
4·0% NH_4Cl	C	0·230	0·226	1·7	76·2

distilling off liberated formaldehyde to be estimated iodometrically[10,11]. A selection of these results is given in Table VI. Some samples were also boiled for 40 min. in 20% ammonia, which is claimed to remove uncombined formaldehyde very effectively[12], and the aldehyde content was again estimated. The results of these tests, a small selection of which is given in Table VII, were not completely conclusive. Since, however, small proportions only of formaldehyde are removed by boiling ammonia, the formaldehyde content remaining in the cellulose after extraction should be there mostly in the combined and not in the polymerised form. There was some indication that residual combined formaldehyde could be responsible for lowered water retention, but the conditions of drying and baking seem to have a greater influence. Were the connection straightforward, then the formaldehyde content should rise as the water retention falls.

NITROGEN CONTENT

So far an attempt has been made to connect the chemical effects of combination of formaldehyde with cellulose (blocking of hydroxyl groups and cross-linking) with lowered capacity for water absorption and swelling. This relation may be obscured by the presence of formaldehyde combined in a urea–formaldehyde condensate but not attached to the fibre-substance. It is seen that, after soaping and regulated acid extraction, the relation is indicated but not very clearly or consistently. This inconsistency may come from a neglect of the urea component of any condensate in which the fibre-substance participates.

Since it was found that acid extraction did not remove all nitrogen-containing substances, the nitrogen content of acid-extracted specimens was determined and the nitrogen calculated as urea. A selection of these results is given in Table VI.
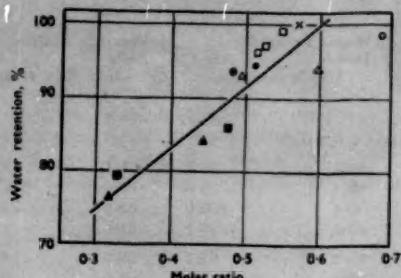
FIG. 17— Effect of Molar Ratio of Urea to Formaldehyde upon Water Retention after Acid Extraction, for Different Catalysts
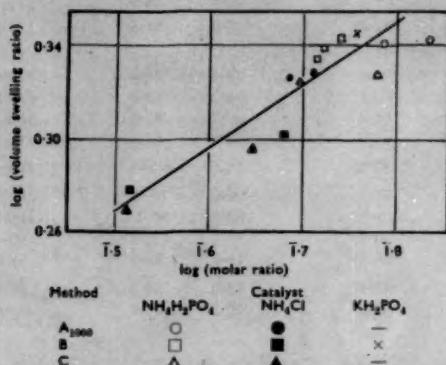
FIG. 18— Effect of Molar Ratio of Urea to Formaldehyde on Volume Swelling Ratio after Acid Extraction, for Different Catalysts

In Fig. 17 water retention is plotted against the molar ratio of urea to formaldehyde, and in Fig. 18 the logarithm of the volume swelling ratio against the logarithm of this molar ratio. There is some scatter, but a consistent relation is indicated. No correction has been made for the variation of total nitrogen content just mentioned. Among the different specimens there have been different conditions of condensation, e.g. variations in acidity, which are known to affect the molar ratio of urea to formaldehyde in the resin condensate. The relation must therefore be regarded as approximate only. The indications are that it is cross-linking by polymer chains in which urea participates rather than blocking by methylenation which restricts water-uptake.

PHYSICAL PROPERTIES

It is on such criteria as recovery from creasing, stiffness, and freedom from tendering in the finished cloth that the practicability of a given resin treatment is judged. The results of physical tests on treated samples are collected in Table VIII.

From these results, taken with those based on measurements of water retention, the general effect of drying and baking conditions (assuming the application of a standard proportion of the pre-condensate in the first step) can be summarised as follows—

A— Favouring High Crease Resistance

(1) With potassium dihydrogen phosphate as catalyst— (a) Static air conditions during drying and baking. (b) High drying temperature.

(2) With ammonium salts as catalysts— Drying and baking in a current of moving air, i.e. low ambient formaldehyde concentration.

B— Tending to give Unsatisfactory Crease Resistance

(a) With ammonium salts, for static-air methods (B and C) an increasing proportion of catalyst. (b) Increased water vapour content of air in Method A. (c) A high formaldehyde vapour content in the air in static methods.

Bending length increases as crease resistance falls; i.e. crease resistance and stiffness are antagonistic. The variations in bending length, however, seem to be important only when crease resistance is low.

On the whole, any treatment which favours high crease resistance .will tend to maintain or increase the tensile strength, since both are assumed to be related to the degree of cross-linking. With catalysts which can liberate strong acids, e.g. ammonium salts, rise in temperature, unventilated drying and baking, and high resin content all tend to diminish tensile strength and extensibility simultaneously. This may be due chiefly to depolymerisation of the cellulose, but the rigidity caused by extended polymerisation in the resin itself could well make an important contribution.

Discussion

The various aspects, mechanical and chemical, of processes designed to diminish the tendency of cellulosic fabrics to shrink or to crease (i.e. designed to improve dimensional stability) have been so voluminously discussed that it is very difficult to give a résumé here. For the assistance of the reader, before a final discussion of the results of the present work, a series of references will be given.

PHYSICAL ASPECTS OF CREASE RESISTANCE

Here the comprehensive discussions of Buck and McCord[13], Cameron and Morton[14], and Landells[15] should be studied. It is accepted that the treatment must increase the elasticity of the fibre, but the relative parts played by cross-linkage of the fibre molecules and by packing out of the hollow spaces in the fibre by growing polycondensate structures are still a matter for discussion.

RESISTANCE TO SHRINKAGE
(DIMENSIONAL STABILITY)

It is generally agreed that woven structures containing latent strains become actively unstable and shrink upon wetting, more because of the disturbance caused by lateral swelling of the fibres than by axial shrinkage [9,16,17], and that ester formation [18-20], acid-catalysed reactions with formaldehyde [21-25], and reactions with formaldehyde or glyoxal together with other reagents [14,15,26-31] all lead to a diminished tendency to shrinkage in the treated fabric because they diminish the capacity for water absorption and consequent swelling.

TABLE VIII

Method of Drying* and Baking	Catalyst Concn. (%)	R_t (%)	Crease Recovery (%)	Bending Length	Breaking Load (g.)	Extension at Break (%)
Untreated	—	—	36·7	1·30	192	23
POTASSIUM DIHYDROGEN PHOSPHATE AS CATALYST						
A_1000	1·0	(Water only)	—	—	194	21
	1·0	13·7	—	—	183	15
	1·0	14·6	64·5	1·52	—	—
A_1000w	1·0	12·4	62·2	1·40	—	—
A_500	1·0	14·2	66·1	1·42	—	—
A_550	1·0	14·5	69·4	1·37	197	17
B	1·0	19·9	68·3	1·42	206	17
C	1·0	18·4	69·4	1·39	192	16
A_1000*	1·0	18·4	66·2	1·48	—	—
B*	1·0	22·6	73·9	1·40	—	—
C*	1·0	22·8	70·0	1·54	—	—
AMMONIUM DIHYDROGEN PHOSPHATE AS CATALYST						
A_1000	0·5	23·1	72·2	1·50	186	19
	1·0	26·2	76·2	1·52	179	17
	2·0	25·1	76·7	1·46	197	13
	4·0	24·5	71·4	1·40	173	12
B	0·5	24·5	62·3	1·40	160	14
	1·0	24·8	64·2	1·54	171	14
	2·0	26·2	54·0	3·18	134	13
	4·0	26·1	39·5	5·18	105	9
C	1·0	24·6	61·4	1·78	142	13
	4·0	24·2	36·7	4·54	88	11
AMMONIUM CHLORIDE AS CATALYST						
A_1000	0·5	24·3	71·2	1·48	150	13
	1·0	24·8	70·5	1·42	143	13
	2·0	23·3	70·8	1·48	137	12
	4·0	20·8	70·8	1·40	84	12
A_1000w	4·0	22·1	41·7	2·51	159	12
B	0·5	23·9	58·1	1·89	139	13
	1·0	23·8	51·7	2·58	140	13
	2·0	24·1	40·6	4·35	165	12
	4·0	24·5	31·7	4·26	86	8
C	1·0	22·2	36·1	4·26	120	12
	4·0	24·2	33·4	5·02	43	9

*The drying temperature was 60°C. for all samples except those marked with an asterisk (*), for which it was 80°C.

CHEMICAL BEHAVIOUR OF FORMALDEHYDE

The properties of formaldehyde in solution and in the vapour phase most relevant to the present discussion are— (1) The tendency to form a hydrate CH_2O,H_2O in dilute solution at higher temperatures, which hydrate is in equilibrium with a growing concentration of the vapour as the temperature rises. (2) The tendency to form polyoxymethylenes of probable constitution $HO\cdot[CH_2\cdot O]_n\cdot H$ as the temperature falls and the concentration increases, the products becoming sparingly soluble in water as n exceeds 3. Formaldehyde in the polyoxymethylene form is available on heating for reaction and, incompletely, for reversion to the gaseous monomer. With high concentrations in the solution the insoluble paraformaldehyde results. Heating solid paraform is a useful device for producing formaldehyde vapour. Like other aldehydes, formaldehyde can suffer change, catalysed by alkalis and by acids, into mixtures of the corresponding alcohol and carboxylic acid—

$$2H\cdot CHO + H_2O \rightarrow CH_3OH + H\cdot COOH$$
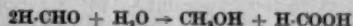
ACTION OF FORMALDEHYDE ON CELLULOSE

This is a much discussed subject. There is one fairly clear preliminary distinction, viz. that direct interaction of the reagent with hydroxyl groups in cellulose to form acetals, hemiacetals, or ethers requires acid as a catalyst. Alkaline catalysts encourage a less well defined action, in which polyoxymethylenes, with some tenuous connection with the cellulose, are formed in the fibre-substance. They do cause some modification of the dyeing and mechanical properties. It will be recalled that, even with acids present, there were indications of this kind of action in the present investigation.

The effects of combination between cellulose and formaldehyde have been widely discussed [32-36], and many of the discussions have centred round the relative importance of cross-linking and methylenation of adjacent hydroxyls on the same glucose residue. A most interesting and detailed investigation by Wood [12] estimates the probability of internal ether formation, a possibility which has been more or less discounted by other workers [37-39].

In view of the results of the present work, the work of various investigators [43-42] on the effects of temperature and vapour concentration upon the degree of combination of aldehyde with cellulose is immediately interesting. There emerges a picture which shows a store of formaldehyde, present as a self-polymer, being built up within the fibre on drying or heating at temperatures below about 100°c. and with low concentrations of acid catalyst—especially in the presence of high vapour concentrations—and these deposits breaking down to furnish reagent for combination with the cellulose as the temperature is raised and the acid concentration is increased [37]. An increase in the acidity, e.g. increasing concentration of the catalyst, has been shown to lead to resin with a lower molar ratio of urea to formaldehyde [37(a)]. By analysis of specimens, after acid extraction of the bulk of the resin condensate, this molar ratio is shown to have increased for that fraction of the condensate still present (Table VI). The values obtained usually exceed appreciably the molar ratio in the precondensate (1 : 1·67) for treatments where formaldehyde is liberated and either kept as vapour and in a polymerised form in the system (Method B) or taken away from the system (Method A). When the total resin contents are examined, the molar proportion of formaldehyde is, as might be expected, always found to be much less than the corresponding value for the precondensate. The values obtained for the molar ratio of urea to formaldehyde can therefore be fully explained only by supposing that some of the residual formaldehyde, viz. that portion not combined with residual nitrogen, has formed a cross-link and is present as methylenecellulose. The predominance of pure formaldehyde links, as assumed above, is reflected in the increasing values of the molar ratio of formaldehyde to urea, accompanied by a steady decrease in the water retention. The observation that the resistance of acid-extracted specimens to solution by cuprammonium hydroxide increases with increasing ratio of formaldehyde to urea is further evidence in the same direction. Incidental evidence for cross-linking between cellulose chains comes from reported results by Vogel [44] and Boulton [45], in which depolymerisation of the cellulose, largely ascribable to the acid used as a catalyst, does not lead to a corresponding drop in tensile strength. An account of modification of cellulose by the direct action of formaldehyde vapour [46] is also cogent to the present work.

CONDENSATIONS OF UREA AND FORMALDEHYDE

The general story of urea–formaldehyde condensations is found in the wider literature of plastics chemistry [47-50]. There are a variety of alternatives for the course of polycondensation, and which shall predominate depends on— (a) molecular ratio of urea to formaldehyde, (b) pH, (c) time, and (d) temperature. At low temperatures and in solutions which are not acid the simple well defined mono- and bis-hydroxymethylureas—

$$(H_2N \cdot CO \cdot NH \cdot CH_2OH \text{ and}$$
$$HO \cdot CH_2 \cdot NH \cdot CO \cdot NH \cdot CH_2 \cdot OH)$$
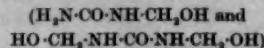
are formed. The action of heat and acid catalysts causes polymerisation, and bishydroxymethylurea as it participates liberates formaldehyde and water [51-55]. The extent to which this liberation forms part of reversible condensation reactions, and therefore the extent to which they may be encouraged or inhibited by a high external formaldehyde concentration, still seems to be a matter for speculation.

UREA–FORMALDEHYDE TEXTILE FINISHES

The distinctive feature of the anti-crease finishes in which urea–formaldehyde or analogous polycondensates are used appears to be that the condensate must be so distributed that it exists substantially within the fibre and neither cements fibres or threads together nor forms hard continuous films within the yarn and cloth structures. It is thus essential that the molecules of the precondensate should not be too large to penetrate into the fibre structure, and this has led to various detailed prescriptions for controlling the degree of condensation when impregnating baths are made, for ensuring full dispersion, and for swelling the fibre [36,56-59]. Staining methods followed by visual or electron microscopy to demonstrate the distribution of resin within the fibre are readily capable of giving ambiguous or misleading indications, but the most reliable do seem to show the presence of substantial proportions of resin within the interior of effectively treated fibres [15,60-69].

Once the condensation has taken place, the relation between the polycondensate molecules and the fibre molecules does not seem yet to be capable of certain definition [14,15,70,71]. The simplified extremes among the alternatives are (a) cross-linking, (b) stuffing. The former postulates an attachment of two cellulose chains to the same polycondensate molecules—

$$\text{HC—O—P—O—CH}$$
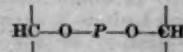
the latter the formation of extended polycondensates in spaces between the cellulose chains without attachment necessarily existing.

The results obtained for residual nitrogen on the specimens after acid extraction show that some resin condensate remains firmly attached to the cellulose. It is not yet possible to state definitely the effect of resin attached in this way upon water absorption as compared with the effect of forming pure methylene ethers. The condensation is catalysed by the presence of acid, and so is the

hydrolysis of the condensate. The decrease in nitrogen content with increasing concentration of the catalyst (Table VI) appears to be due to continuing hydrolysis, so that there is a smaller proportion of acid-resistant resin in the fibre. For ammonium phosphate, the effect is first seen at a concentration of 2%.

APPLICABILITY OF PRESENT RESULTS TO INDUSTRIAL PRACTICE

Most of the immediate implications of the present results have been commented upon when the results themselves have been described. It now remains to consider how much information useful in operation has been obtained.

Drying

Normally drying will take place on a hot-air jet dryer or stenter, and the conditions would be best represented by the A methods, with concentrations of water vapour and formaldehyde kept low in the ambient air. Methods B and, particularly, C represent extreme cases leading to accumulations of aldehyde, which are not likely to be met in practice, but which might be approached in systems of recirculated air drying. There is little evidence that the accumulation of formaldehyde vapour at the drying stage alone affects the results of condensation, but it can lead to an accumulation of polyoxymethylene compounds on the cloth, representing a greater available supply of form-aldehyde when the baking stage is reached. The effect of restricted ventilation on the development of acidity when an ammonium salt is used as a catalyst has not yet been closely studied, as this calls for a special experimental treatment.

Baking

Restricted ventilation in drying plus a high ambient concentration of formaldehyde at the baking stage are feasible industrial conditions, whether a molten-metal bath is used or not. It has been seen that evolution of water vapour and of formaldehyde are essential steps in the resin formation, and it has been claimed that excess of free formaldehyde retards condensation and leads to discontinuities in the resin structure [72, 73]. Where the acidity of the catalyst is low (1% KH_2PO_4) and direct combination between form-aldehyde and cellulose is unlikely, treatments in an unventilated system seem to retard condensation, as shown by relatively high moisture regain and water retention (Fig. 14 and 15). It has been claimed also that high partial pressure in the baking chamber retards evolution and, though the resin deposit may be greater, it is less fast to washing [74]. This has not been substantiated in the present experiments.

The presence of water vapour in the reaction vessel does, in fact, lessen the stability of the formaldehyde vapour, and it causes greater formation of polyoxymethylene reserves (Method C, Fig. 6). There is evidence that these can occur both on the cloth and on parts of the baking chamber during drying, and can give a boost to the vapour concentration on baking. The general consensus of evidence is, however, that, in addition to the formation of polymer deposits, encouraged by drying at low temperatures and by restricted ventilation and leading to an enhanced evolution of formaldehyde vapour on entry into the baking stove, some of this additional formaldehyde vapour comes from the polymerisation itself. Even ventilation at the highest air-speeds is not sufficient to clear this vapour away as fast as it is formed.

Fixation of Resin

The conditions of drying and baking must be considered in conjunction with the choice of catalyst. Drying and baking in moving air (Fig. 9 and 11) leads to a lower fixation when potassium dihydrogen phosphate is the catalyst. With the relatively moderate acceleration of condensation, solidification during drying and in the early stages of baking has been relatively slow, and migration of the reactants to the surface has been much in evidence. With the ammonium salts as catalysts, solidification takes place earlier, total fixation is greater, and then the beneficial effects of a moving air stream in removing moisture and formaldehyde and in increasing the acidity are reflected in resin deposits which are faster to washing.

Although no work has yet been done on the subject, different systems of heating during baking might have other effects on the fixation and the distribution of resin. Where there is moving heated air, heat is brought to the cloth by convection; the air is a low-temperature source of low heat content, so that drying and condensation will tend to become superficial, and migration of precondensate will be encouraged. Any arrangement which increases the proportion of radiant heat received should tend to uniform drying and setting through the thickness of the cloth.

Physical Properties of Treated Cloth

In general terms, the finisher requires an anti-crease treatment to give a permanent resistance to creasing with a minimum rise in stiffness. In these experiments, there is a general distinction between the effects of A treatments, which give a relatively soft finish, and those of B and C treatments, which with the more powerful catalysts give stiff finishes. This agrees with the observations of Marsh, who states that high concentrations of formaldehyde lead in general to "hard" effects, as does increased water vapour pressure.

The observed stiffness may be due to— (a) excessive cross-linking and methylenation compared with "packing" between the cellulose molecules; (b) some migration of the resin to the surface to form, in the end, a hard thin crust with a soft inside, due to slow drying.

Molten-metal Baths

The indications, leading up to direct experiments, of the possibility of using metal baths surrounding the cloth are summarised as follows—

(1) With an intermediate drying stage omitted, the cloth would go through the precondensate and into metal at polymerising temperature. Conditions would be between those of Methods B and C. The cloth would be surrounded by high equilibrium concentrations of water and formaldehyde vapours. A weakly acid catalyst would be required; otherwise, great stiffness, loss in strength, and poor crease resistance are to be expected.

(2) Drying in a ventilated drier before baking in a closed system has been shown to lead to— (a) high resin content, (b) good resistance of resin to removal by washing, (c) satisfactory crease resistance, and (d) low stiffness. This suggests that a procedure of impregnation, ventilated drying, and baking in molten metal holds greatest promise. A weakly acid catalyst only would be needed, always a desirable feature, and there would probably be a marked economy in formaldehyde consumption.

* * *

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[70] Marsh, *op. cit.*[17], p. 421.
[71] Wood, *J. Textile Inst.*, **37**, 335 (1946).
[72] Ellis, *op. cit.*[17], p. 598.
[73] Pollak, *Chem. Abs.*, **23**, 1227 (1929).
[74] Wall, *Text. Manuf.*, **64**, 164 (1938).
[75] Wagner and Pacsu, *Text. Research J.*, **22**, 12 (1952).
[76] Steele, *ibid.*, **25**, 545 (June 1955).
[77] Best-Gordon, J.S.D.C., **69**, 46 (1953).

Discussion

Dr. F. C. WOOD: We at Tootal Broadhurst Lee Co. experimented with hot molten metal and hot oil in that order, in April 1934 and October 1937 and also subsequently. The idea must have originated, I fancy, in a perusal of the history of our iniquitous and rude forefathers, who hotted up their unsuspecting enemies with boiling oil and molten lead. (You cannot change inhuman nature, and we are even more iniquitous and ruder now with atomic fission.) We were not satisfied with either of these methods of curing at the time. We put through the hot-oil or molten-metal baths both wet and dry hydroxymethylurea-impregnated fabrics and would never have dreamed of conducting such an investigation as the authors now present. If you fall in love with a girl, it would seem to be a little odd to take a five-year course in anatomy and physiology before getting married. While you were so occupied, somebody else would marry the girl.

We married the impregnated cloth to the molten metal, so to speak, and the union was not profitable. The conclusions Alvsaker and Turner put under the title "Molten-metal Baths" were the obvious alternatives immediately to apply.

Mr. TURNER: I did not know that Dr. Wood and his colleagues tried molten metal before it was suggested by other people, since, so far as I know, this is the first time that the fact has been communicated. But unlike falling in love, technical development work should have a purely factual and not an emotional basis. Having tried his various runs through molten metal and the like and having found the results unsatisfactory, what more can Dr. Wood do? If he has the true scientific attitude and still wants to know why they misfired, presumably he, too, will have to abandon a rather inflexible experimental system and adopt one in which the different factors can be more readily isolated. He may then obtain information which will tell him how his molten metal ought to work or, if it does not, suggest other methods of working. I think that there must always be a great temptation when one has had a detailed acquaintance with a process for a very long time to do a certain amount of *post-hoc* rationalisation of some stages of its history.

Dr. WOOD: The second matter I comment on is the sentence: "Detailed investigations by Wood estimate the probability of internal ether formation, a possibility which has more or less been discounted by other workers." Whilst I have never disagreed with the cross-linking mechanism in the cellulose–formaldehyde reaction as a possible theory, I maintain that it has not yet been proved beyond doubt.

Consider the following facts—

(1) Glyoxal is assumed to cross-link with neighbouring cellulose chains and this necessarily assumes the molecule of glyoxal accomplishing twice at the same time what I assume is possible *once* with formaldehyde. You admit that two camels can go through the eye of a needle at the same time, and refuse me the theory that one can go through on his own more easily!

(2) Soda cellulose can be dried down to a low moisture content, and it can then be methylated with dimethyl sulphate, etc. It has just the same physical properties as methylenated cellulose— reduced swelling, low water absorption, etc.— and no cross-linking is possible here. Similarly, you can obtain high-swelling methylenated celluloses by conducting the methylenation with the cellulose chains pushed apart by large amounts of water, as Dr. T. H. Morton knows from his own patents.

The American work on cellulose–formaldehyde of Wagner and Pacsu[75] and later Steele[76] is unconvincing. The former authors have not read my 1931 and 1933 papers with attention, as they attribute formulations to me which I ruled out, and the latter makes the astounding inference that the number of free hydroxyl groups in the product is less than in the original cellulose, so that cross-linking must have occurred. This conclusion is not warranted by the evidence they submit.

The assumption of chemical formulation from physicomechanical properties is justifiable only if backed up by organic chemical evidence both in cellulose and in protein studies, and I submit that there are some awkward facts which are not compatible with the simple cross-link theory. I left the constitution of my monomethylene-cellulose (17·2% OCH_3) for the university laboratories, as I had other fish to fry.

Mr. TURNER: I have read the passage in our paper that Dr. Wood cites, and I still feel that it should stand. It will be seen that this is not an expression of our opinion. To give this on our short acquaintance of anti-crease work, unless we had some very precise data in hand, would not be justified. In a survey, however hurried, it does seem to give a reasonably accurate indication of what some other workers of standing believe. To cite the example of glyoxal seems to represent a kind of reasoning which Dr. Wood later deplores, since, both sterically and in its possibilities of reaction, glyoxal seems to be only a very approximate analogue of formaldehyde. I would like to hear what Dr. Morton has to say on the possibilities of formaldehyde cross-linking *versus* methylenation. We have mentioned both as possible explanations for modifications in the properties of the cellulose which persist after a large proportion of the polycondensate has been removed.

Dr. T. H. MORTON: The evidence for cross-linking of cellulose in the urea–formaldehyde process, in deference to Dr. Wood, is purely inferential, but is not less well grounded for that. Consideration of various cross-links, e.g. those noted with melamine–urea and acetone–formaldehyde resins, leaves little doubt that adjacent cellulose molecules are linked by methylene and more complicated bridges.

Mr. J. S. INGHAM: We have been investigating the use of the Best-Gordon staining test[77] for assessing crease-resisting finishes. We have some

evidence that, not only does this test show the location of the resin, but it shows also the degree of condensation of urea–formaldehyde and/or the combination of formaldehyde with cellulose. I would therefore like the authors' comments on the following two experiments—

(1) We took cloth treated with ·the urea–formaldehyde condensate, using as catalysts—

    (a) Ammonium phosphate

    (b) Ammonium chloride

    (c) Ammonium thiocyanate

We baked these together in the normal way for $2\frac{1}{2}$ min. at 150°c., and half of each length was then given a second baking. The staining test showed that, in the case of the thiocyanate, the twice baked sample was stained to a lesser intensity than the once baked sample, whereas with the chloride and phosphate the reverse was the case.

(2) We treated four pieces by the normal phosphate procedure, washed one immediately, and let the other pieces stand on the batch for three days. After washing, staining tests were carried out on all four pieces, and it was found that the piece washed off immediately had a much lighter stain than those washed off after standing for three days. The pieces on the batch showed roughly the same degree of staining, but the piece in the middle of the batch was slightly darker than the others on the outside of the roll.

Under the conditions of the first experiment the thiocyanate was probably giving more condensation on double baking, whereas the chloride and the phosphate on double baking were tending to depolymerise the resin, and/or bring about more reaction between formaldehyde and cellulose than did the thiocyanate. In the second experiment, the piece washed after baking the urea–formaldehyde

was in a higher state of condensation than the piece left standing for three days. It was also possible that in the latter case some formaldehyde was combined with the cellulose.

Mr. TURNER: Without further investigation, I find it difficult to give a very precise answer. To follow the possibilities, one may say that any conditions in which steady polycondensation of the precondensate took place should cause a steady fall in the coloration after prolonged baking times. If, however, the presence of a strong acid as catalyst causes first polycondensation and then dissociation of the condensate, as suggested by the results in Fig. 12 when Method A is used, one might easily find a greater coloration after a prolonged or a repeated baking than after an initial short one. The catalysts used are all salts of strong acids, and, although ammonium phosphate starts condensation at a lower temperature but does not develop quite so high a final acidity, there seems to be no reason why thiocyanic acid should not give similar results to hydrochloric acid. Were all these salts compared at the same molar concentration? The detailed study of pH changes with drying, baking, different kinds of catalyst, moisture content of the system, etc. should prove very illuminating*.

With respect to the second experiment, one would think that the heavier stain with the samples that had stood would denote a reversal of condensation by free acid from the catalyst, encouraged by heat retention in the batch. All these suggestions are speculation and are based on a very convenient theory, for if after long treatments staining is low, progressive condensation is the answer; if it is high, depolymerisation can be invoked.

* Since the meeting I have discussed this matter with Mr. Best-Gordon, and he agrees that this is as far as we may safely go.—H.A.T.

The Dyeing and Finishing of Cellulose Triacetate Yarns and Fabrics

A. MELLOR and H. C. OLPIN

The physical and textile properties of cellulose triacetate fibres are such that fabrics made from them, or containing substantial proportions of them, may be permanently set in much the same way as are nylon and Terylene. The dyeing properties of triacetate yarns are compared with those of secondary acetate yarns, both alone and in admixture with other fibres.

I—Introduction

During recent years widespread interest has been aroused in the properties of cellulose triacetate. In retrospect, it may be seen that this is a natural development from the success attained, over a period of years, in the dry-spinning of secondary acetate, with its breakaway from established techniques, its new dyeing methods, and the new textile processes and properties to which it gave rise. The acceptance of these processes and properties smoothed the path for the introduction of the newer polymers, so that the return of triacetate became a logical next step when so many of the problems which had restricted its earlier progress had been solved.

The revival of interest in cellulose triacetate may be illustrated by reference to three papers which were published in the forties. The first, in 1942, by Baker, Fuller, and Pape[1], dealt with the crystallinity of cellulose esters; the second, in 1949, by Dr. G. Hinz[2], dealt with the technology of cellulose triacetate; and the third, also in 1949, by Dr. R. Work[3], described the effects produced by crystallinity and orientation on the X-ray diagrams of cellulose triacetate filaments.

The first paper[1] showed that, when cellulose triacetate is allowed to solidify near the fusion temperature, it attains a high degree of crystallinity and, in this condition, gives rise to a typically crystalline X-ray powder diagram; whereas when the molten triacetate is quenched at either 20°C. or −75°C., the X-ray pattern indicates a random disposition of the molecular chains, particularly about their long axes. It was further shown that crystallinity could be developed in quenched samples by subjecting them to annealing treatments, the effectiveness of the treatment increasing with time and temperature. After heating for 2 hr. in air at 200°C. crystallinity was still very imperfect, whereas after 2 hr. at 225°C. it closely approached that of the sample solidified near the fusion temperature.

The article by Hinz[2] pointed out that the early production of cellulose triacetate failed to fulfil expectations, mainly because of its poor thermal stability, which was due to traces of the sulphuric acid catalyst used in the esterification. He showed that, in the light of modern knowledge and by the choice of suitable catalysts, acetylation could be carried out so that no trace of harmful material remained, and the triacetate produced would be really stable.

Dr. Work's paper, which was presented at the Annual Meeting of the Textile Research Institute in November 1948, reviewed the results of research studies on cellulose triacetate and secondary acetate made over a period of twenty years by the staff of the Celanese Corporation of America and their consultant organisation, Fabric Research Laboratories Inc. The paper included X-ray diagrams of triacetate filaments in their normally spun state, i.e. with only low degrees of crystallinity and orientation, and then of the same material after being held for some time at a temperature just below its melting point, when a substantial increase in crystallinity was observed. The fact that this work was carried out on filaments instead of on powder represented an important technical advance.

Investigations on this subject, during the above period, in the laboratories of British Celanese Ltd. showed that, by the use of special treatments, it was possible to obtain X-ray diffraction photographs of cellulose triacetate yarns showing the highest degree of crystallinity combined with orientation yet found in any textile fibre. An example illustrating this condition is shown in Fig. 1. It will be seen that the diagram is exceptional in the number and the sharpness of the spots. A certain amount of detail has been lost in reproduction, but on the original negative a total of 206 spots can be counted.

It was also found during the course of this work that the combination of high crystallinity and orientation illustrated in Fig. 1 was neither necessary nor desirable in a yarn intended for general textile purposes, and that a much lower degree of orientation was preferable if combined with a suitable level of crystallinity, or orderliness of the internal structure. Examples of the controlled low degree of orientation which is found satisfactory in a textile yarn are given in Fig. 2 and 3, which are X-ray diffraction photographs of filaments extracted from Tricel fabrics before and after the application of an annealing or setting treatment such as is described later in this paper.

In Fig. 2, which refers to a Tricel yarn as spun, the lengths of the arcs indicate that the orientation is only moderate; while the lack of detail, in comparison with Fig. 1, shows that the degree of internal regularity of structure is of a much lower order. Fig. 3 shows that the orientation has been increased only slightly by the heat-treatment, but that the crystallinity has markedly increased, as is indicated by the greater number of resolved arcs.

It was further found that increased crystallinity in a triacetate yarn was associated with a number of special properties— increase of ironing temperature, capability of being set, etc.— most of which were highly desirable in themselves but brought in their train a number of corresponding processing problems, which the dyer and finisher, as is usual in such matters, was called upon to solve.

While this work was in progress, in the period from 1949 onwards, signs of ever increasing activity with triacetate became evident in the United States and Britain, and to some extent in Germany, culminating in the almost simultaneous launching in 1954–1955 of triacetate yarns and fibres under the names of *Arnel* (Celanese Corpn. of America), *Courpleta* (Courtaulds Ltd.), *Trilan* (Canadian Celanese Ltd.), and *Tricel* (British Celanese Ltd.). The authors' experience of triacetate yarns and fabrics has been mainly acquired with Tricel, for which reason this product is specifically referred to in the remainder of this paper. Other forms of cellulose triacetate may be expected to show generally similar behaviour, except for minor variations.

GENERAL PROPERTIES OF TRICEL YARNS AND FIBRES

For convenience of reference on the part of dyehouse chemists and textile technologists, we summarise below the more important chemical and physical properties and textile characteristics of Tricel fibres. All properties refer to heat-set materials.

II— Processing of Tricel Fabrics

The processing of fabrics made from triacetate yarns proceeds initially along conventional lines. A thorough scour should be given to remove size, oil, and dirt, the method of scouring being determined by the fabric construction and the nature of the equipment to be used for dyeing.

Two very important points should be noted here— Tricel fabrics are very resistant to alkalis in the strengths normally used for scouring and dyeing; and they are resistant to delustring in boiling soap baths. High temperatures and alkaline scour baths can therefore be used with safety and will facilitate the removal of oil and dirt.

HEAT-SETTING OF TRICEL FABRICS

Heat-setting treatments may be given either before or after dyeing, either with dry heat at temperatures between 190°c. and 250°c. or with

TABLE I

Summary of the General Properties of Tricel Fibres

GENERAL CHEMICAL PROPERTIES

Combined acetic acid content	61·5–62·5%
No. of acetyl groups per glucose residue ...	3
Unit molecular weight	288

ACTION OF ORGANIC SOLVENTS

Soluble in— Chloroform, methylene chloride, formic acid, glacial acetic acid, dioxan (slow), m-cresol (slow)

Swollen by— Acetone, ethylene dichloride, trichloroethylene*

Unaffected by— Methylated spirit, benzene, toluene, xylene, dry-cleaning solvents such as white spirit, carbon tetrachloride, and tetrachloroethylene (perchlorethylene)

GENERAL PHYSICAL PROPERTIES

Density at 20°c.	1·32 g./c.c.
Melting point	300°c.
Softening point	220–225°c.
Glazing point (of fabrics under stationary iron)—	
Not set	170–180°c.
Heat-set	240°c.
Thermal coefficient of bulk expansion—	
Below 60°c.	0·00044/°c.
Above 120°c.	0·00105/°c.
Second-order transition temperature (for rate of increase in temp. of 20°c./hr.) ...	97°c.
Specific heat—	
20–100°c.	0·32 cal./g./°c.
20–200°c.	0·34 cal./g./°c.

TEXTILE CHARACTERISTICS OF STANDARD TRICEL YARN OR FIBRE

Tenacity†	1·2–1·4 g./denier
Tenacity (wet)...	0·7–0·8 g./denier
Breaking stress†	15·2 kg./sq.mm.
Ratio of wet strength to dry strength ...	~0·6
Extension at break†	20–25%
Extension at break (wet)	30–40%
Young's modulus†	44 g./denier
Toughness (work of rupture)† ...	0·23 g./denier
Knot tenacity†	1·0–1·2 g./denier
Loop tenacity†	1·0–1·2 g./denier
Moisture regain of heat-set fibres† ...	2·5–3·0%
Water imbibition of heat-set fibres, at 1000 *g* (centrifuging method at 100% R.H.) ...	10–11%

* Trichloroethylene should not be used for dry cleaning.
† Standard conditions— 65% R.H., 70°F.

wet steam at temperatures between 120°c. and 145°c. It is important to note that, in contrast to the nylons and Terylene yarns, Tricel yarns are not subjected to any orienting process by cold stretching after spinning, and thus there is no tendency for Tricel fabrics to shrink or contract during heat-setting.

(1) Dry-heat Setting

Tricel fabrics may be dry-heat-set by any of the methods found applicable to nylons or Terylene. All three materials become somewhat plastic under dry-heat-setting conditions, but Tricel differs from the others in that it has little or no tendency to shrink. Internally heated drum machines should prove very satisfactory for woven fabric, provided that tension is kept low. Where a

stenter is used to carry the fabric through the heating zone, it is sometimes necessary to support the fabric with a carrier blanket, or more economically by the use of a balanced flow of hot air, suitable conditions of treatment being exposure to a temperature of 220°c. for 20 sec.

(2) Steam Setting

Because Tricel fabric does not contract during heat-setting, roll setting can be carried out in moist steam in a Sanderson-type steamer without danger of obtaining width variation from inside to outside of the roll. Another factor which must be taken into account is that Tricel yarn when wetted extends slightly. If dry fabric in roll form is submitted to moist steam, this slight extension will be revealed as small furrows or wrinkles in the fabric, which become permanently set, so spoiling the finished appearance. The scoured fabric should therefore be batched, free from creases, whilst still wet or damp, on to the perforated steaming tube. The damp rolls are then entered into a pressure steamer, the vessel is evacuated, and steam is allowed to enter through the perforated tube until a gauge pressure of 20 lb. per sq. in. (125°c.) is achieved. This pressure is maintained for 30 min. The fabric is then cooled by blowing air through the system, and taken out for further processing.

(3) Hot-water Setting

Another variation of setting treatment is to submit the fabric to water under pressure at temperatures similar to those used for steam setting, e.g. 125°c. Such conditions may occur in high pressure beam-dyeing machines, pressure dye jiggers, and the new Barotor (DuP) machine.

III— Dyeing

CLASSIFICATION OF DYES

The dyeing of Tricel fibres and fabrics will normally be carried out with disperse dyes. In Table II representative disperse dyes are classified according to their behaviour at different temperatures. The first group will naturally be chosen for normal requirements whenever conditions will allow.

DYEING ISOTHERMS

(1) Comparison of Tricel and Secondary Acetate Rayon Fibres

Fig. 4–7 give dyeing isotherms for four typical disperse dyes dyed on ordinary acetate rayon yarn at 80°c., compared with unset, steam-set, and dry-heat-set Tricel yarn dyed at 98°c. These graphs show that, in all cases, ordinary acetate rayon has the greater dye uptake, and that dyes vary amongst themselves in their behaviour towards Tricel yarn as compared with ordinary acetate rayon yarn.

(2) Effect of Swelling Agents

Fig. 8 and 9 show the effect of various swelling agents on the uptake of SRA Brilliant Blue IV (BrC). In this work the diethyl phthalate, tris-

TABLE II
Disperse Dyes for Tricel

1. GOOD OR VERY GOOD SUBSTANTIVITY AT 90°c.

SRA Fast Golden Yellow XIII (BrC)
SRA Fast Golden Yellow VIII (BrC)
SRA Golden Yellow IX (BrC)
Eastman Fast Yellow 8GLF (TE)
Eastman Fast Yellow 2R GLF (TE)
Duranol Brilliant Yellow 6G (ICI)
Dispersol Fast Yellow G (ICI)
Amacel Yellow CW (AAP)
SRA Fast Golden Orange III (BrC)
SRA Orange III (BrC)
SRA Fast Pink II (BrC)
SRA Rubine B (BrC)
SRA Scarlet III (BrC)
SRA Fast Red VII (BrC)
SRA Red VIII (BrC)
Serisol Fast Red 3BL (YDC)
Celanthrene Violet BGF (DuP)
Duranol Brilliant Violet B (ICI)
Duranol Violet RN (ICI)
SRA Fast Heliotrope I (BrC)
Eastman Fast Violet 3R GLF (TE)
SRA Brilliant Blue IV (BrC)
Serisol Dark Blue B (YDC)
Artisil Direct Blue GFL (S)
Duranol Blue GN (ICI)
SRA Fast Violet Blue FSI (BrC)
SRA Navy Base VI (BrC)
SRA Fast Black IV Base (BrC)

2. MODERATE SUBSTANTIVITY AT 90°c. BUT GOOD SUBSTANTIVITY AT 98°c.

SRA Rubine IX (BrC)
Eastman Fast Blue GLF (TE)
Serisol Fast Blue Green B (YDC)
Duranol Blue 2G (ICI)

3. MODERATE SUBSTANTIVITY AT 98°c.

Dispersol Yellow 3G (ICI)
Eastone Fast Red GLF (TE)
Eastone Fast Brilliant Red 2B GLF (TE)
Cibacet Brilliant Scarlet RG (Ciba)

4. SUITABLE FOR APPLICATION ABOVE 100°c.

Eastone Fast Red GLF (TE)
Eastone Fast Brilliant Red 2B GLF (TE)
Eastman Fast Blue GLF (TE)
Interchem Acetate Blue BGLF 40 (IC)
Cibacet Sapphire Blue 4G (Ciba)
Supracet Golden Orange GR (LBH)

chloroethyl phosphate, and tributyl phosphate were emulsified in an aqueous solution of a sulphated fatty alcohol and added to the dyebath as required. Phenol, being soluble in water at the temperature of dyeing, did not require emulsification. The curves indicate clearly the superiority of diethyl phthalate over the other swelling agents tested, particularly at low concentrations. It is a valuable assistant, not only for pure Tricel fabrics, but also for the Tricel–wool fabrics which are dealt with later.

Fig. 10–12, together with Fig. 4, show the results of a similar study, in slightly greater detail, of the behaviour of Eastone Fast Red GLF, in the presence of the various swelling agents mentioned above. This series shows again the remarkable

efficacy of diethyl phthalate in increasing the substantivity of Tricel yarns, the other two swelling agents— phenol and trischloroethyl phosphate— being relatively ineffective.

Diethyl phthalate has a modifying action on cellulose triacetate. The difference in the yarn denier after treatment (Table III) is partly due to absorption of diethyl phthalate, but mainly due to shrinkage.

TABLE III
Effect of Diethyl Phthalate on Cellulose Triacetate Yarn

(Treatment at 80°c. for 2 hr. in dyebath)

Diethyl Phthalate (g./litre)	Denier	Tenacity* (g./denier)	Extensibility (%)
0	88	1·20	14·6
5	108	1·10	20·0

* At 65% R.H.
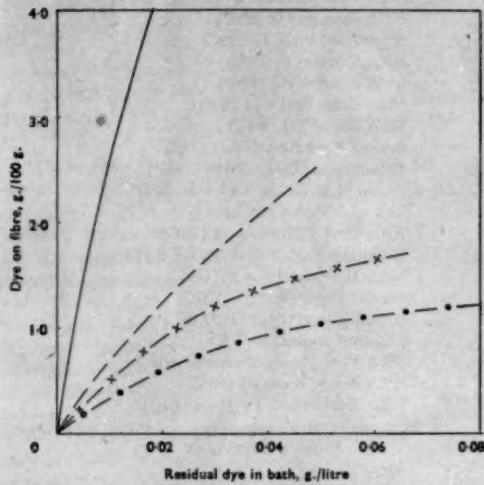
FIG. 4— Eastone Fast Red GLF
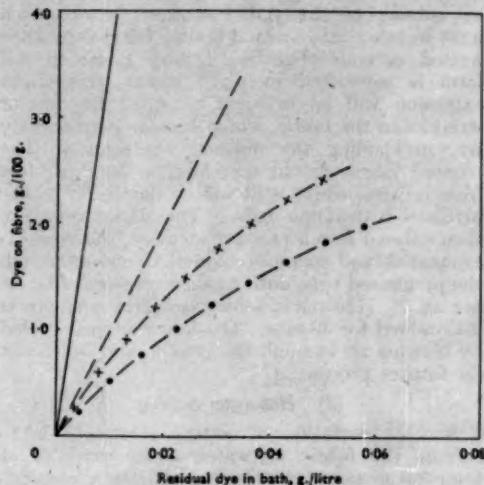
FIG. 6— Supracet Fast Red G
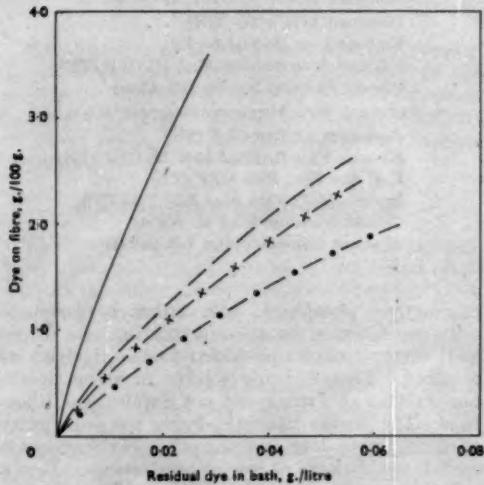
FIG. 5— SRA Brilliant Blue IV 300 powder
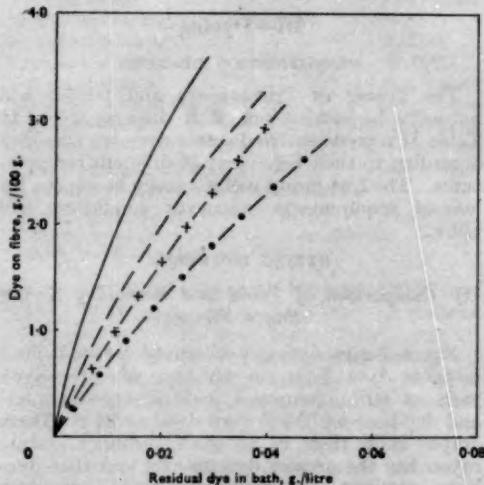
FIG. 7— SRA Golden Yellow IX 300 powder

——————— Normal acetate yarn (dyed at 80°C. for 2 hr.)

– – – – – Tricel yarn, unset

–×—×– Tricel yarn, steam set

–●—●– Tricel yarn, dry heat set

FIG. 4–7— Tricel Yarn dyed at 95–96°c. for 2 hr. in 50 : 1 Bath
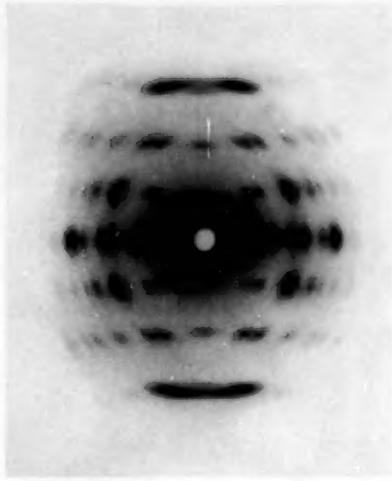
Fig. 1— X-Ray Photograph of highly Crystalline Triacetate,
Dry-heat-annealed at 270°c. under Tension
(X-ray beam perpendicular to axis)
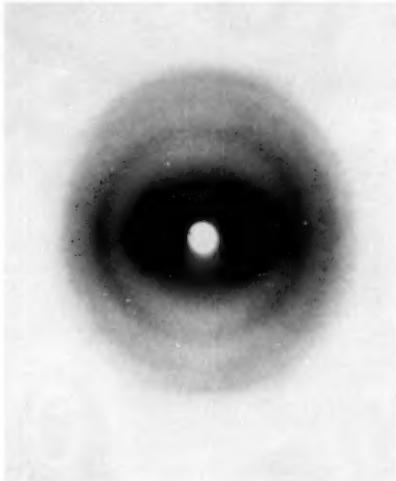
Fig. 2— Tricel Filaments from Fabric NF 2001, not set
(X-ray beam perpendicular to axis)

Fig. 3— Tricel Filaments from Fabric NF 2001, heat-set at
220°c. for 20 sec. (X-ray beam perpendicular to axis)
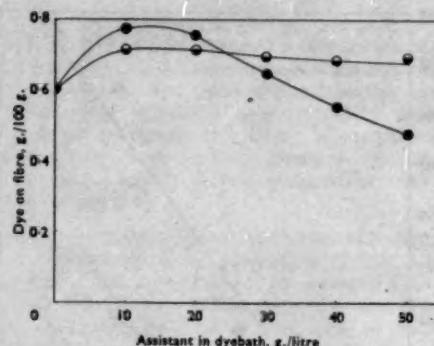
FIG. 8— 1·0% SRA Brilliant Blue IV 300 powder
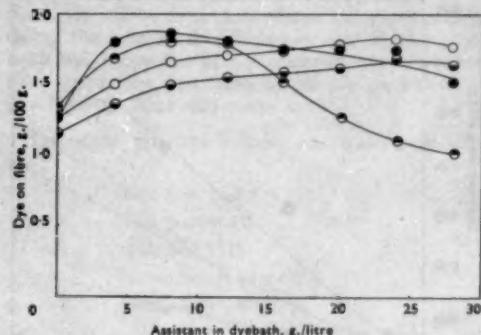
FIG. 9— 2·5% Brilliant Blue IV 300 powder

● Diethyl phthalate   ◔ Phenol   ○ Trischloroethyl phosphate   ◑ Tributyl phosphate

FIG. 8 and 9— Tricel Fabric dyed at 80°C. for 2 hr. with Various Assistants
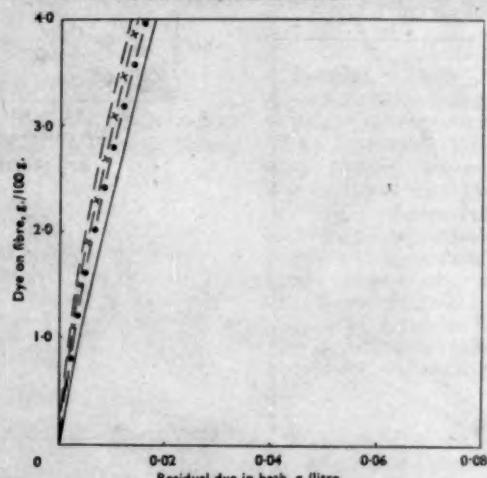
FIG. 10— Diethyl Phthalate (5 g./litre)
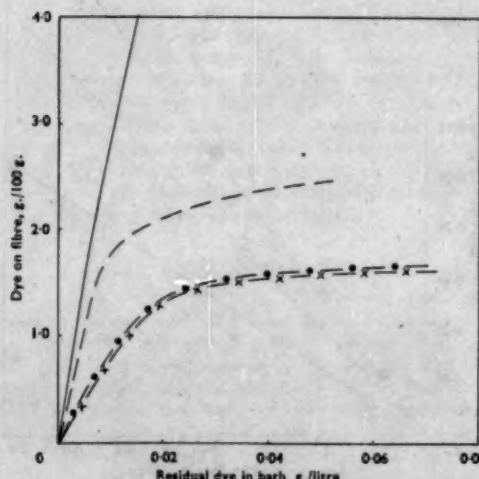
FIG. 11— Phenol (10 g./litre)

FIG. 12— Trischloroethyl Phosphate (5 g./litre)

——— Normal acetate yarn   -×—×- Tricel yarn, steam set
– – – Tricel yarn, unset   -●—●- Tricel yarn, dry heat set
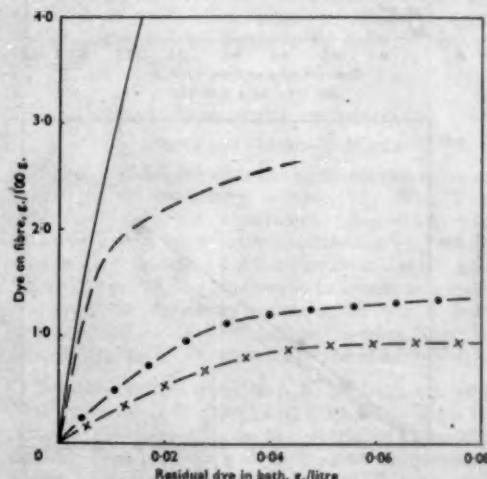
FIG. 10–12— Eastone Fast Red GLF dyed with Various Assistants at 80°C. for 2 hr.
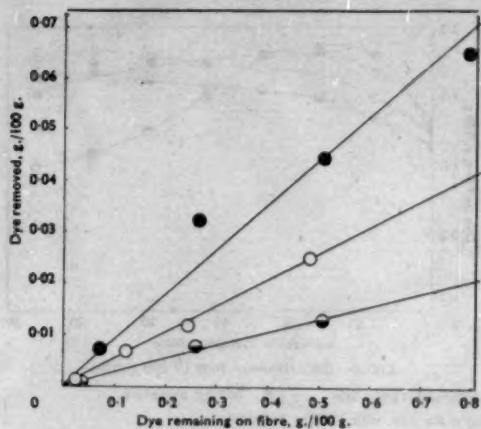
FIG. 13— SRA Fast Red VII
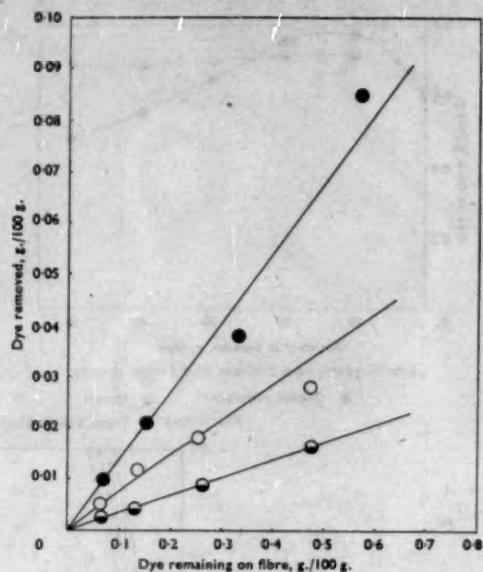
FIG. 14— SRA Scarlet III
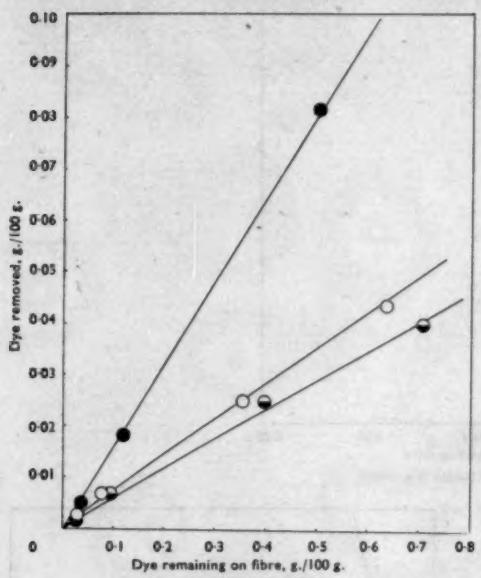
FIG. 15— SRA Red VIII
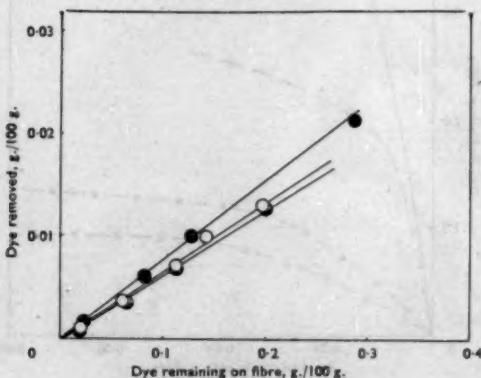
FIG. 17— Duranol Blue 2G

FIG. 16— Artisil Direct Blue GFL

● Secondary acetate fabric   ○ Tricel fabric   ◑ Heat-seat Tricel fabric

FIG. 13–17— Fastness to Washing of Dyed Tricel
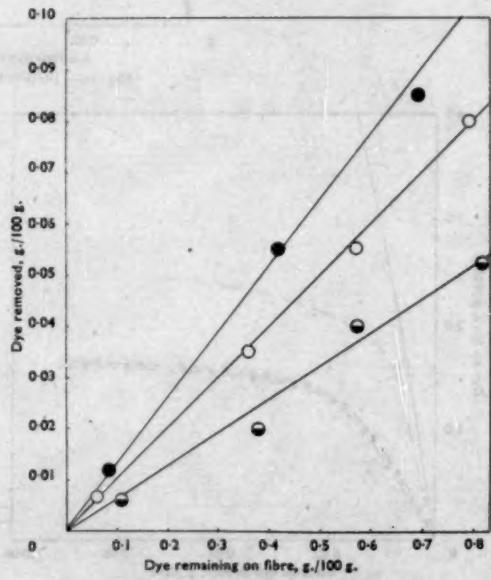
These data conform to the general picture that water-soluble swelling agents like phenol are of only limited value, while the water-insoluble compounds are efficacious, but each has a limiting useful concentration which is approximately that of maximum uptake by the fibre. When present in excess, they form a third phase in the dyeing system, and are in active competition with the fibre for the dye.

The above information indicates the value of dyeing assistants in the production of dark colours on Tricel, but it should not be assumed that the assistants selected for the preceding illustrations are necessarily the best or even used in the best possible way. Apart from cost, availability, and simplicity of usage, the means of removing swelling agents from the fibre and the effectiveness of such removal will be important factors in making the final choice.

FASTNESS OF DISPERSE DYES ON TRICEL

In general, the fastness values of disperse dyes on Tricel fibres are similar to those on secondary acetate rayon.

(1) Light

Most dyes show the same order of fastness to light on Tricel materials as on secondary acetate. In the choice of dyes to meet specified requirements the dyer can safely rely on his experience with normal Celanese yarns.

(2) Gas Fading

Dyes which show good immunity on secondary acetate show a similar fastness on Tricel, whilst those which require protection should be given protection on Tricel materials.

Both substantive and non-substantive inhibitors may be used to obtain protection, but where substantive materials are used, e.g. Anti-acid 3546 (B·C), Serisol Inhibitor 30 (YDC), Inhibitor GF (ICI), or GF Inhibitor BASF (BASF), it should be remembered that these products have the same characteristics as disperse dyes. Adequate protection is given when not less than 1% of the active ingredient is present on the fibre, and the quantities used should be adjusted accordingly.

(3) Washing

The fastness to washing of disperse dyes on Tricel as compared with secondary acetate yarns forms a very interesting study. All the dyes so far examined show increased fastness on Tricel, and are better still on heat-set Tricel. The differences in fastness vary considerably, however, from dye to dye, as will be seen from Fig. 13–17, which show the results of subjecting dyeings of various depths to soaping treatments in soap (2·5 g./litre) in a 40 : 1 bath at 60°c. for 30 min. In each graph, the amount of dye in the scour bath is plotted against the amount of dye on the fibre. It will be seen that, within the experimental error, the relationship between dye in the scour bath and dye on the fibre is linear in every instance, thus furnishing examples of simple partitions of dye between fibre and scour bath.

The dyes for which data are quoted in Fig. 13–17 are—

> SRA Fast Red VII
> SRA Scarlet III
> SRA Red VIII
> Artisil Direct Blue GFL
> Duranol Blue 2G

Duranol Blue 2G differs markedly from the remainder in that its fastness to washing, which is good, is only slightly better on the Tricel samples than on secondary acetate.

(4) Alkali

Fastness to alkali is of particular interest, since it has been found that some dyes which are sensitive to alkali on secondary acetate are unaffected on Tricel materials. For example, the dyes SRA Fast Golden Yellow XIII (aminoazobenzene→phenol) and SRA Fast Golden Orange I (aniline →α-naphthylamine→phenol), both of which have long been discarded for use on secondary acetate owing to their colour changes to red and purple respectively, even when very low concentrations of alkali are dried in the fabric, show little or no change on Tricel. The first of these two dyes— SRA Fast Golden Yellow XIII— should be a useful addition to the range of dyes applicable to Tricel.

In the past, it has been necessary to condemn the practice of obtaining navy blues by coupling bases with 2:3-hydroxynaphthoic acid owing to their sensitivity to alkali. On Tricel, however, the fastness of such navy blues to alkali is quite satisfactory, though fastness to light is not all that can be desired.

FAST COLORATIONS ON TRICEL
(1) Developed Colours— Blacks

Black is obtained with the same combination on Tricel as on secondary acetate, viz. SRA Fast Black IV, or its equivalent, diazotised and developed with 2:3-hydroxynaphthoic acid. Owing to the slow uptake of 2:3-hydroxynaphthoic acid by the aftercoupling process, it has been necessary to devise a modified technique in which both components are applied before entering into the diazotising bath. A working recipe is as follows—

The material is dyed in a 30 : 1 bath set with Pentrosan A2 (1 c.c./litre) and SRA Fast Black IV Base 300 powder (6% on the weight of material). Dyeing is commenced at 50°c., the temperature being raised to 95-98°c. during 30 min. and maintained at this value for 60 min. longer. After washing off, the fabric is entered into a fresh bath at 60°c. containing 2:3-hydroxynaphthoic acid

(2% on the weight of material) dissolved in one-quarter of its weight of caustic soda and a little water, the pH of the liquor being then adjusted to 3·0 by addition of formic acid. The temperature is raised to 95°c. during 15 min., and held at 95–98°c. for 30 min. before washing off.

For diazotisation a bath is made up containing 6% sodium nitrite and 24% hydrochloric acid (32°Tw.) on the weight of material, and the fabric worked for 30 min. at 20°c. After washing off it is treated for 15 min. at 60°c. in Adinol T High Conc. (Fine Dyestuffs & Chemicals Ltd.) (0·5 g./litre).

The developed colour technique has not been fully exploited, but in view of the fact that simple developers such as phenol can be used with the expectation of adequate fastness to wet processing, there are considerable possibilities in this field.

(2) Azoic Combinations

These can be applied to Tricel in much the same way as to secondary acetate rayon. It is necessary, however, to work at pH values of about 7, the percentage uptake of coupling component decreasing rapidly with rise in pH. Useful combinations for various colours are indicated in Table IV.

These azoic combinations have very satisfactory colour stability and fastness to wet processing, which is understandable since it is possible to carry out the final soaping at the boil and obtain, if not full aggregation (since the colours do not in every case correspond to those on cellulosic fibres), a degree of stability adequate for all normal purposes.

(3) High-temperature–Slow-dyeing Disperse Dyes

In practice, the azoic combinations do not cover all the requirements of the textile industry, there being notable gaps on Tricel as on other fibres. It is possible, however, partly to fill these gaps on Tricel by use of the high-temperature–slow-dyeing disperse dyes. For many purposes these are of sufficiently high all-round fastness, including freedom from migration during washing, provided that they are applied correctly, and they are essentially free from surface-deposited dye.

The possibilities in this field are illustrated in Table V, which gives the fastness to staining, on to Tricel fabrics, of a number of dyes applied by the diethyl phthalate method. These dyes may be applied by the above technique to yarn and loose stock in the usual package-dyeing machines at temperatures up to 100°c. If, however, high-temperature dyeing equipment is available, allowing the use of temperatures up to, say, 130°c., the "carrier" becomes unnecessary.

TABLE IV
Light Fastness of Azoic Combinations on Tricel

Naphtol	Base	Nearest B.C.C.* Shade	Light Fastness
BRIGHT TRICEL			
AS–G	Fast Garnet GBC	Buttercup BCC 53	4
AS–BG	Fast Orange GC	Spectrum Orange BCC 57	5
AS–BS	Orange Base Ciba V	Nasturtium BCC 96	3–4
AS–BG	Fast Red RC	Union Jack Red BCC 210	4–5
AS–BG	Fast Red B	Cherry BCC 185	4
AS–BG	Fast Garnet GBC	Peony Red BCC 37	6
AS–BS	Fast Garnet GBC	Medici Crimson BCC 240	5–6
AS–BC	Fast Corinth LB	Garnet BCC 160	4
AS–LB	Fast Red RC	Mace BCC 73	4–5
AS–LB	Fast Red GG	Golden Brown BCC 74	5
AS–LB	Fast Garnet GBC	Terra Cotta BCC 133	6
AS–LB	Cresidine→cresidine	Horse Chestnut BCC 134	4
†AS–DB	Cresidine→cresidine	Nigger Brown BCC 20	6
SEMI-DULL TRICEL			
AS–G	Fast Red B Base	Lemon BCC 52	3–4
AS–G	Fast Garnet GBC	Saffron BCC 54	4
AS–BS	Fast Red GG	Nasturtium BCC 96	4
AS–OL	Fast Red RC	Cherry BCC 185	3
AS–BS	Aminoazobenzene	Cardinal BCC 186	5
AS–LT	Fast Red B	Claret BCC 36	4–5
AS–BO	Fast Corinth LB	Garnet BCC 160	3
AS–BG	Fast Garnet GBC	Ruby BCC 38	5
AS–LB	Fast Scarlet GG	Almond Shell BCC 67	4
AS–LB	Fast Scarlet TR	Golden Brown BCC 74	4–5
AS–LB	Fast Garnet GBC	Rust BCC 58	4
AS–LB	Fast Red B Base	Horse Chestnut BCC 134	5
†AS–DB	Cresidine→cresidine	Nigger Brown BCC 20	6

* British Colour Council

† Diethyl phthalate used as assistant

TABLE V
Fastness to Washing of Slow-dyeing Disperse Dyes
(S.D.C. Test No. 2, staining of Tricel fabric)

Dye	Depth (%)	Wash Fastness
Amacel Yellow CW	1·0	5
	2·5	4–5
Eastman Fast Yellow 2R GLF	1·0	4–5
	2·5	4–5
Eastman Fast Yellow 8GLF	1·0	5
	2·5	4–5
Eastone Fast Red GLF	1·0	4
	2·5	3
Eastone Fast Brilliant Red 2B GLF	1·0	5
	2·5	4–5
Eastman Fast Violet 3R GLF	1·0	3
	2·5	2
Celanthrene Violet BGF	1·0	4
	2·5	3
Eastman Fast Blue GLF	1·0	5
	2·5	4–5
Interchem Acetate Blue B GLF 40	1·0	4–5
	2·5	4

The above table shows that careful selection of dyes is necessary, but the fastest of these dyes are believed to be satisfactory for obtaining a limited number of popular shades for two-colour garments. The superiority of Tricel over secondary acetate fabric in this respect is illustrated by the examples in Table VI.

TABLE VI

Colour Combination	S.D.C. Wash Test No. 2 Staining on—	
	Secondary Acetate	Tricel
BOTTLE GREEN–IVORY		
3% Amacel Yellow CW	3	4–5
3% Eastman Fast Blue GLF		
CHOCOLATE BROWN–IVORY		
2·5% Amacel Yellow CW		
1·2% Eastone Fast Red GLF	2	4–5
3·0% Eastman Fast Blue GLF		

DYEING METHODS

(1) Preliminary Treatment

Before subjecting Tricel fabrics to any wet processing treatment it is desirable to stabilise or relax the material by methods which are well known in connection with the treatment of secondary acetate rayon. These treatments differ according to fabric construction, and may vary in severity from merely passing the fabric in open width through water to steeping in soap solution at the boil.

(2) Jig Dyeing

Those fabrics which show a tendency to crease when run in rope form, e.g. satins, twills, and taffetas, must be dyed on the jig or on the beam. Dyeing should be carried out at the boil with selected disperse dyes, since dye absorption and penetration are thereby improved. Closed dye jigs are advocated, so as to minimise temperature differences between the lists or selvedges and the middle of the batch.

C

As the fibre is resistant to delustring, the use of temperatures above 100°c. must also be considered, for in this way high-temperature slow-dyeing dyes can be satisfactorily applied. Equipment for this purpose is limited for the time being to high-pressure jigs such as are supplied by Sir James Farmer Norton & Co. Ltd. and Benninger & Co. Ltd. These machines are expensive and require ample floor space, but it is expected that satisfactory results will be obtained on most plain fabrics after manipulative experience has been gained. The need for such experience arises from the fact that the fabric is removed from outside control, apart from the ability to modify tension.

The fact that high-temperature dyeing is permissible, without lustre modification and without undue plasticity, indicates that beam dyeing is a distinct possibility. For such dyeing high-pressure package-dyeing machines may be adapted. The fabric is dyed as warps are dyed, by winding on to a perforated roller under correct tension control so as to ensure freedom from creases and undue expansion when under liquor pressure.

(3) Winch Dyeing

Winch dyeing will normally be used for Tricel fabrics whenever the fabric construction is suitable, e.g. for warp-knitted fabrics of all types, and for woven fabrics where the weft twist and denier are such as to prevent sharp creases from being formed when the fabrics are run in rope form over the winch roller. Most fabrics made from staple fibre blends may also be satisfactorily dyed in rope form on the winch.

The dyebath will be prepared with the usual assistants found advantageous for the levelling of disperse dyes, e.g. soap, Turkey Red oil, and synthetic detergents and dispersing agents. If the fabric has been "preset", dyeing may be carried out at or near the boil, for the presetting process confers definite resistance to creasing under such dyeing conditions. For "unset" fabrics, lower temperatures are advised as a matter of safety, and 90°c. may be the upper limit.

(4) Subsidiary Treatments
(a) Bleaching

Undyed fabrics made from Tricel yarns may become slightly yellow as a result of heat treatment, but any of the usual bleaching agents, viz. acid or alkaline hypochlorite, peracetic acid, hydrogen peroxide, or sodium chlorite, may be used to obtain an excellent white. Sodium chlorite is preferred as a general-purpose bleaching agent, since it can also safely be used for blends of Tricel with other fibres. Where the initial discoloration is slight, fluorescent brightening agents having substantivity for Tricel fibres are effective in achieving "whiter whites".

(b) Stripping

As with most other fibres, it will sometimes be necessary to strip and redye to correct an initially faulty dyeing. Rescouring will only serve to remove a small amount of colour owing to the high wash fastness. Where heavy depths require

drastic stripping, zinc formaldehyde-sulphoxylate at pH 3–4 may be used for azo dyes, whilst sodium chlorite, acidified with formic or oxalic acid, will deal with the anthraquinone blues. In most cases, the fabric after stripping may be yellow or light orange, and it should be noted that such residual colour has a low fastness to light. As with secondary acetate, finely divided carbon may be used in a soap bath to give a mild stripping treatment.

DYEING TRICEL IN ADMIXTURE WITH OTHER FIBRES

Secondary acetate in admixture with other fibres gives rise to processing problems in connection with general launderability. It is probably on this account that this field of fibre usage has not been very widely exploited. With the availability of Tricel in staple form, many fabrics can now be produced which have excellent wash fastness and stability, this being especially so after the heat-setting process. Because of the Tricel content of such fabrics, special finishes such as moiré, embossed effects, and pleating effects can be given which are very durable in wear.

(1) Tricel–Secondary Acetate Mixtures

Fabrics made from mixtures of these two fibres will normally be dyed with disperse dyes having substantivity for both at the maximum safe temperature for secondary acetate. The latter will usually be dyed the deeper colour, and differences in hue may also be evident when mixtures of dyes are used, owing to differences in the distribution of the individual dyes between the two fibres. The limitations of these methods are obvious, and in addition the optimum setting conditions for Tricel cannot be applied.

A limited number of cross-dyed effects may be obtained by exploiting the fact that Tricel fibres have little affinity for the water-soluble anionic dyes which have affinity for secondary acetate.

(2) Tricel–Cellulose Fibre Mixtures

The dyeing of Tricel–cellulose mixture fabrics, whether made from continuous-filament yarn or from spun yarns composed of blends of these fibres in staple form, presents no more difficulty than similar fabrics containing secondary acetate, since those dyes which are resisted by the secondary acetate also show excellent resists on Tricel yarns.

It has already been stated that Tricel materials show greatly increased resistance to caustic alkalis. This property enables a wide range of vat and sulphur dyes to be applied to the cellulosic component of these mixtures, under conditions of normal usage, without staining or impairing the physical properties of the Tricel component.

With 50 : 50 blends of Celafibre and Fibro an anti-crease finish is customary. When the Celafibre is replaced by Tricel, however, the heat-set fabric has appreciable crease-resistant properties in its own right, and no real benefit results from the application of an anti-crease finish. Further increase in the Tricel content will, of course, further improve its anti-crease properties.

(3) Tricel–Wool Mixtures

Many interesting and desirable fabrics have been made from blends of Tricel and wool. To dye the wool and leave the Tricel unstained is a simple matter, there being a wide choice of acid- and neutral-dyeing acid dyes available. The disperse dyes which are used for the Tricel fibres, however, stain the wool appreciably, even when dyeing is carried out at the boil, as is possible with such blends.

The use of dyeing assistants such as diethyl phthalate for promoting uptake of disperse dye by the Tricel fibre has been found to be particularly efficacious in Tricel–wool blends, because it enables full colours to be obtained on the Tricel with relatively slight staining of the wool.

A suitable dyebath is made by emulsifying diethyl phthalate in a non-ionic dispersing agent such as Dispersol VL (ICI) or Pentrosan A2 (Glovers) so that the dyebath contains 3 g. diethyl phthalate and 1 g. dispersing agent per litre, the dyeing being carried out at a liquor ratio of 40 : 1 for 30 min. at the boil.

For this work it is desirable to use the high-temperature slow-dyeing dyes, which are of very satisfactory fastness to soaping and are unaffected by the subsequent clearing treatment. After correct application, i.e. after sufficient time has been allowed for full penetration, the mixture fabric may be scoured for, say, 30 min. at 50°C. in order to reduce the staining of the wool to a minimum, without affecting the colour on the Tricel.

In these Tricel–wool blends the optimum setting temperature for the Tricel cannot be applied, since the wool would thereby be damaged, but in any case the Tricel content will confer excellent durable pleating properties on such fabrics.

(4) Tricel–Nylon and Tricel–Terylene

These fibre combinations will not present a great deal of difficulty where pale and medium solid shades are required, but problems will arise regarding fastness, since the same dye can show quite different light and wash fastness on the two fibres, and sometimes a different colour. It has not, so far, been possible to carry out any systematic investigation with these fibre mixtures, so that it is not yet possible to make recommendations. With regard to setting, the conditions selected will be dictated by the nylon or the Terylene, which are more easily damaged by heat than is Tricel.

PRINTING TRICEL FABRICS

(1) Disperse Dyes

The simple printing pastes which have proved satisfactory for applying disperse dyes to secondary acetate have been found to need modification for Tricel fabrics, the introduction of solvent-swelling agents being necessary. The following recipe gives prints which compare favourably with prints of the same dyes on secondary acetate by normal techniques—

	Parts
Dye, 10% milled paste	20
Zinc thiocyanate	10
Triacetin	5
Nafka Crystal Gum 40% (Scholten)	35
Water	30
	100

After printing and drying, the goods are steamed for 1 hr. at 220°F., and then thoroughly washed in cold water.

The dyes listed in Table VII have been successfully applied in full colours. Where possible, those dyes which belong to the high-temperature slow-dyeing range should be selected for use, since they are so very much faster to washing on Tricel, and soiling of the unprinted ground during washing off is comparatively mild and controllable.

TABLE VII

Dyes for Printing Tricel

SRA Yellow IV
SRA Golden Yellow IX
SRA Scarlet II
SRA Scarlet III
Eastone Fast Red GLF
Duranol Red X3BS
SRA Rubine IX
Serisol Blue Green B
Eastman Fast Blue GLF
SRA Brilliant Blue IV
SRA Fast Violet Blue FSI

The above recipe and dye selection do not necessarily represent the final word, but they do indicate that already Tricel can be printed satisfactorily with disperse dyes under normal processing conditions to give prints having very desirable fastness properties.

(2) *Vat Dyes*

With the usual alkali-metal carbonate–Formosul (Br) printing pastes the colour yields with selected vat dyes are poor and the usual modifications give little or no improvement. Manofast (Hardman & Holden's formamidinesulphinic acid) as the reducing agent, however, has given promising results with the following recipe—

	Parts
Dye	15
Manofast	5
Urea	10
Polyethylene glycol	6
Zinc thiocyanate	10
Gum tragacanth	40
Water	14
	100

Table VIII lists dyes applicable by this method.

These prints were steamed twice for 15 min. each time at 220°F. in a John Wood steamer, washed thoroughly, and then oxidised in 2 g. sodium dichromate and 2 c.c. acetic acid per litre at 50°c. for 15 min. Oxidation was slow and incomplete when cold, but proceeded rapidly at 50°c.

TABLE VIII

Vat Dyes for Printing Tricel

Caledon Golden Yellow GKP (ICI)
Caledon Jade Green XS (ICI)
Ciba Blue 2B (Ciba)
Ciba Red 2B (Ciba)
Indanthren Blue GG (FBy)
Indanthren Scarlet B (FBy)
Durindone Scarlet 2B (ICI)
Durindone Red BS (ICI)
Ciba Deep Printing Black BD (Ciba)

Samples of prints from the above were soaped at 60°c. and at 95°c. for 30 min. Apart from Ciba Red B, which underwent a marked change in hue, they were little affected by soaping at the higher temperature. Should any surface colour be present after soaping, a mild alkaline hydrosulphite treatment will immediately effect its removal.

IV— Finishing

Finishing processes for Tricel fabrics follow the established procedure for secondary acetate, and wherever possible pure finishes are advocated.

A silicone finish will be found efficacious for giving a durable wash-fast proofing on Tricel, as would be expected from its hydrophobic nature. It will often be convenient, when such a finish is required, to combine the silicone curing process with that of heat-setting, thus completing both processes in a single heat-treatment.

Two points should be noted arising from the application of a silicone finish on Tricel. Firstly, improved resistance to abrasion may be expected; and secondly, fabrics of low construction tend to slip or fray where piece joinings are made.

The general tendency today is for firm, dry finishes. In this respect, Tricel, without assistance, comes closer to this objective than does secondary acetate. Where softer finishes are required, cationic agents such as Ceranine H 39 (S), Gemex Z7 (Gemec), etc. are useful.

Conclusion

The success or otherwise of a new fibre— and Tricel is new in the sense that it has not previously been exploited commercially— depends upon its intrinsic properties as a textile and the uses which can be made of these properties in the industry as a whole. In practically all of these uses dyeing and finishing are essential processes, and the problems presented by Tricel fabrics are somewhat unusual, though they all fall within the scope of a well equipped dyehouse. If this contribution proves useful in any way in assisting Tricel yarns to find their rightful place in the textile industry, the authors will be amply rewarded.

*   *   *

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Discussion

Mr. R. F. YORK: Have any other phthalates been tried, and if so what was the reason for choosing diethyl phthalate?

Mr. MELLOR: A number of the lower alkyl phthalates were tried. The diethyl ester was readily available in quantity, and since it proved efficacious in initial tests, it was chosen for experimental work.

Mr. H. R. HADFIELD: It is seen from Fig. 8 that, under winch dyeing conditions, 20–30% (on weight of fabric) of diethyl phthalate produces an increase in absorption of only about 30%. Practically, is the use of this high amount of carrier of economic advantage and to be recommended?

Mr. MELLOR: Fig. 8 should be studied in conjunction with Fig. 9–12 of the same series. Since SRA Brilliant Blue IV comes in Group 1 of Table II, viz. dyes which have good substantivity unaided at 90°C., it would not be expected to benefit greatly by the use of a carrier.

Fig. 8 and 9 show that amounts of carrier, e.g. diethyl phthalate and tributyl phosphate, in excess of that absorbed by the fibre result in a third phase which is in active competition with the fibre for dye, and hence they produce a lighter dyeing. The value of diethyl phthalate for assisting dye uptake is shown in Fig. 10–12, where a high-temperature slow-dyeing dye such as Eastone Fast Red GLF is used.

Mr. HADFIELD: Would you say that an essential property of a carrier is to be readily removed after use?

Mr. MELLOR: Yes, ready removal of carrier from the fibre after use is a very desirable property. The necessity to ensure its complete removal will depend upon the properties of the carrier and its influence on the characteristics of the fibre.

Mr. HADFIELD: Does the use of a carrier affect the crease recovery of triacetate fabrics?

Mr. MELLOR: The use of suitable carriers does not adversely affect crease recovery; in fact, by facilitating slight shrinkage, it could improve crease recovery. Carriers should be so chosen that after dyeing and finishing the physical characteristics of the fibres are unimpaired.

Mr. HADFIELD: The authors rightly point out that deep dyeings of high wet fastness can be produced by the use of very complex, slowly diffusing disperse dyes. These dyes tend to give poor yields when applied in heavy depths, and because of their complex nature are expensive. Are these dyes at present regarded as a practical solution to the problem of producing e.g. a fast navy, in view of the very high cost of dye and dyeing assistant?

Mr. MELLOR: We have indicated the value of carriers for obtaining deep colours. They are, of course, essential for obtaining full shades with the slow-dyeing high-temperature dyes, unless dyeing at temperatures above 100°c. is contemplated, when economic yields can be obtained from a normal dyebath. Navy blues are readily obtained with SRA Navy Base VI, a Group 1 dye, after-coupled with SRA Navy Developer I or III.

Dr. A. F. KERTESS: Can the authors give us some information on the resistance of cellulose triacetate fabrics to trichloroethylene or white spirit used in dry cleaning?

Mr. MELLOR: White spirit is quite satisfactory for dry-cleaning Tricel fabrics. Trichloroethylene should not be used owing to its swelling action on the fibre with consequent bleeding of many dyes into the solvent, but tetrachloroethylene is quite safe. The dry-cleaning industry have been contemplating changing from "tri" to "tetra" for some years [4,5], and it is understood that the production of the latter is already meeting all demands.

Mr. N. F. CROWDER*: Is there a simple and specific spot test for identifying cellulose triacetate, e.g. by the use of a solvent or a mixture of solvents, or by a staining technique?

Mr. OLPIN*: A quick and simple test for distinguishing Tricel from secondary acetate is to steep in cold 40% ammonium thiocyanate for 5 min., rinse lightly, and then immerse in a cold 1% solution of Chlorantine Fast Red 7BL for 5 min. Secondary acetate will be very heavily stained, but Tricel will be virtually unstained. This test can, of course, be carried out on very small samples of material. The Textile Institute publication [6] on the identification of textile materials should also be consulted.

Mr. J. BOULTON: Carriers are, on many grounds, a nuisance, and one hopes that they need not be used, though for some shades they may have to be. Can the authors say what is the effect of the carrier they recommend on the light fastness of the dyes they have used?

* Communicated

Mr. MELLOR: We agree that the use of carriers should be limited as far as possible. They come under consideration chiefly for applying the slow-dyeing high-temperature dyes such as—

> Eastman Fast Yellow 8GLF
> Amacel Yellow CW
> Eastman Fast Yellow 3R GLF
> Eastone Fast Red GLF
> Eastone Fast Brilliant Red 2B GLF
> Eastman Fast Violet 3R GLF
> Celanthrene Violet BGF
> Eastman Fast Blue GLF
> Interchem Acetate Blue B GLF 40

which, owing to their high fastness to both light and gas fading, are so desirable for furnishings. Diethyl phthalate has no adverse effect on the fastness to light of these dyes.

Mr. BOULTON: With reference to the recommendation for a coupled black, was this really fast to rubbing?

Mr. MELLOR: The developed black given in the text can be produced fast to rubbing, but if surface deposition of black does occur, this can be removed quite satisfactorily with an alkaline hydrosulphite treatment at 75–80°c.

Mr. BOULTON: There has been some discussion regarding dye costs for heavy depths: dyeing is thought to be expensive. These are early days for triacetate; when we consider that this relatively cheap fibre will do, as a textile, most of the things the expensive synthetic polymers will do, we should not be concerned so much with the need to use rather more dye than with secondary acetate, but rejoice in the fact that the fibre can, in fact, be readily dyed. Dyeing methods will develop, improve, and settle down to an economical norm over the range of colours and uses.

Dr. C. M. WHITTAKER: Lustron—the first cellulose triacetate on the market—was offered as a resist effect thread, for which the market is inevitably restricted. It was unfortunate in being born before the pioneer dyeing work of Baddiley, Shepherdson, and Holland Ellis had been done on secondary cellulose acetate. It was a reasonable speculation that, if the triacetate could have been dyed on its introduction to the market, secondary cellulose acetate would not have been developed.

Mr. MELLOR: Dr. Whittaker's speculation may well be correct. It would also be reasonable to say that the technical information on heat setting which has resulted from the study of nylon and Terylene will also assist in the processing of cellulose triacetate.

Mr. K. S. LAURIE: The speaker has referred to the dry heat setting of triacetate fabrics giving rise to firmness and yellowing. Would it be of any advantage, as in nylon setting, to use a modified atmosphere instead of air— say, as far as possible a steam atmosphere? This has been found useful and practicable in nylon-setting stenters.

Mr. MELLOR: Since yellowing of triacetate during dry heat setting results from the same cause as that of nylon, namely oxidation, an inert atmosphere during such treatment is to be preferred. If a finisher has such equipment available for nylon, he will naturally use it, to his advantage, for heat-setting triacetate. If not, the slight yellowing may be corrected by a light bleaching treatment with sodium chlorite where necessary.

Mr. J. S. INGHAM: Have the authors any comparative figures of the water imbibitions of Tricel, nylon, and Terylene?

Mr. MELLOR: With regard to water imbibition, Boulton [7] quotes the following—

Courpleta	...	...	15%
Nylon	...	...	12%
Terylene	...	...	5%

whilst in our own paper (Table I) we have given the water imbibition of heat-set triacetate fibre, at $1000\,g$ (centrifuging method at 100% R.H.), as 10–11%.

Mr. INGHAM: Should the Tricel cloth be in the "unset" condition prior to pleating, and has dry heat treatment in pleating any advantages over high-pressure steam?

Mr. MELLOR: It is our opinion that the cloth should preferably be in the unset state, since in such a condition it is more amenable to wet or dry heat treatment. Heat-set fabrics can be successfully pleated, but a higher temperature is required than for unset fabric.

We have not had the opportunity of comparing two similar fabrics pleated by dry heat and by pressure steam. Comparison of fabric set by the two methods leads to the conclusion that dry heat gives a firmer, thinner, and more transparent finish than steam.

Kier Boiling

C. GARRETT

The reasons for tendering in kiers are discussed, and the essential conditions to avoid tendering are given. Steam supply is considered, and operational control is described. The importance of fluidity control is stressed.

The subject of kier boiling is of vital interest to every bleacher, dyer, and printer, and also to other industries which use similar vessels for their process work.

My own deep interest in the subject started soon after the introduction of the fluidity test by the British Cotton Industry Research Association in 1928. The test revealed in measurable terms what was known and feared, the fact that upon occasion tender cloth was produced in the kiering process. The fluidity test, for me, became the keystone of the entire technique of bleaching at all stages of processing. Slowly but surely the pattern became clear as to which conditions are requisite for good results.

It was interesting and instructive to find that when kier boiling practice had been adjusted to give uniform low fluidity results throughout a kier load, two facts emerged. The first was that superior cleanliness of cloth was obtained. The second was that the temperature of the circulating kier liquor corresponded to the temperature of saturated steam at the working pressure of the kier.

It is of interest that during a survey held in Germany in the early 1930s it was found that the incidence of D. & K.* was greatest in cloth boiled in kiers of above 3 tons capacity. The large units were replaced by smaller ones, and today units of around 2 tons capacity are still preferred in Germany.

There are no text-books on the subject of kier boiling, and references to it in books on bleaching are too vague and offer no real guide of operation to the student. My endeavour is to lay before you practical experience that will enable you to understand the basic principles of operation necessary to obtain freedom from chemical degradation during a kier boil. When they have been adopted and are in general use there is no reason why we should not have a British Standard for bleached, dyed, and printed cotton and linen textiles based upon the fluidity test, an objective which I have sought for many years and the prime reason for this paper being put before you.

Kier boiling practice is passed on from one generation to another in each works, and is often a subject of discussion with very wide differences of opinion. To me the boiling of kiers is craftsman's work. It is a very responsible job calling for unlimited patience and intelligent observation, and it deserves sympathetic understanding. The

* "Damaged and kept".

monetary value of a kier full of cloth today is very high indeed; therefore anything that tends to reduce the incidence of tendering is of real worth. A 3-ton kier of good sheeting is worth between £1,500 and £2,000, so that such value should not be processed by chance.

Each bleaching croft possesses an individuality of its own, as the type of plant available and the general "set-up" are not standard. Therefore the practice of kier boiling in works A may, or may not, be successful in works B. The type and the size of kier vary considerably. There are, for instance, puffer pipe circulation, injector circulation, and centrifugal pump circulation, and the last-named can be either belt- or direct-coupled motor-driven. There are also weir-type pump circulation and steam turbine circulation. That is quite a formidable list of variations in circulation. Then there is direct or indirect steam heating, and finally there is the choice of low-pressure or high-pressure boiling. Almost every works has more than one type and size. My experience covers all types from the small 1-ton unit to the large 4-ton unit.

The purpose of this paper is to lay before you suggestions for standardised conditions of operation, which from my experience are essential to good kier boiling practice in all types of kiers. You can then make any modifications necessary in your own works, and try them out.

The object of kier-boiling cloth is to give uniformity of scouring, so that the fabric can be made white with the minimum quantity of oxidising agents. There is a very important factor in addition— the cloth should not be chemically damaged during the process. The measurement of chemical attack is best obtained by the fluidity test, and it is my contention that the top, middle, and bottom of a kier of cloth should have comparable fluidities after boiling.

Patterns for testing should be taken from the same position each time, and this should be adjacent to the first sewing for the bottom, at the last sewing for the top, and an approximation for the middle. In this way daily comparison can be made, and uniformity of sampling is desirable.

A pattern from a lime boil will need careful laboratory preparation such as washing, souring, washing, and then preferably a short soda ash boil followed by thorough washing. One can, of course, wait until after the cloth has been soured and soda-ash-boiled in the works, but this entails delay in getting results.

TABLE I

		Fluidity
Top	...	2·32
Middle	...	2·26
Bottom	...	2·23

A typical set of good results after lime-boiling a cotton cloth is given in Table I. Results below a fluidity of 3·0 can be considered satisfactory after lime boil, sour, and soda ash boil in the case of the lime bleach, and after caustic boil, sour, and caustic boil in the case of the caustic soda bleach. The fluidity results must be uniform throughout the mass. If they are not, then something is wrong.

My paper is based on practical fact, established by daily contact with the problem for more than twenty years. It is all experience with not a single feature in it that cannot be substantiated, and none of it is opinion or conjecture.

The bleaching of cotton and linen piece goods to a high whiteness necessitates the use of caustic alkali boiling, either caustic soda or lime. It is known that tendering does not occur during boiling with sodium carbonate.

It is known that fabrics can be tendered during a caustic alkali kier boil. The reason for this tendering has been the subject of much argument among bleachers for many years, and there are countless theories as to why it happens.

One theory is that too violent circulation causes the liquor to give repeated blows to the cloth and thereby to produce mechanical tendering. In a lime boil where stones had been placed on top of the cloth after filling the kier, the cloth that had been exposed was very tender, but under the stones, where the cloth had been protected from the falling liquor, it was quite strong. This seems to support the theory, but it is not correct.

Another theory is that fridging on the sides of the kier by an intermittent rise and fall of the cloth during boiling causes tendering.

A further theory is that allowing cloth, saturated with lime, to lie exposed so that it dries can cause tendering. But well limed cloth can be dried and, providing that care is taken to wash and sour out the lime, no damage will occur. It is, however, liable to crack when stiff with the lime dried in.

Chemical examination of cloth tendered during a caustic alkali kier boil reveals little of value except by the fluidity test. It is then apparent that more or less serious chemical damage has taken place. This suggests that oxidation has taken place, and the only oxygen that can be present is in the air mechanically taken into the kier by the cloth itself, in the air pockets produced when the cloth is plaited down in the kier, and that between the top of the cloth and the mouth of the kier. Most of the tendering in kiers occurs in the top pieces and it is very often a local affair, referred to sometimes as "tender spots"; the surrounding cloth is perfectly strong.

To prove that air, in the presence of caustic alkali, does cause chemical tendering, the following experiment can be carried out. Tie a piece of grey cloth to the end of a glass tube and, during a caustic alkali boil, have suitable arrangements such as an aspirator or a pump to force air through the tube and thereby pass it through the cloth. The cloth which has been exposed to the air will be more or less tendered, whereas the remainder of the cloth will be perfect. As soon as oxycellulose is produced in this manner, it is immediately dissolved by the caustic alkali, so that it is best to test for the local tendering by the fluidity test. This will show the degree of chemical degradation which has taken place. It can vary enormously depending on the length of time of boiling, strength of caustic alkali, and quantity of air.

It is therefore apparent that the greatest enemy in kier boiling is air, and this air is present—

(1) In the spaces between warp and weft

(2) In the more confined spaces between individual fibres in the yarn

(3) In doubled yarns between the two or more single yarns. The tighter the twist the less the amount of air, but that which is present is more difficult to remove

(4) In the individual fibres themselves

(5) In air pockets produced during plaiting down, and between the top of the cloth and the mouth of the kier.

A large amount of air can be displaced by a steeping process, preferably by overnight steeping. There is overwhelming evidence that an overnight steep is of great benefit. It is very bad practice, in my experience, to singe the cloth, wet it out, and put it into a kier for boiling on the same day.

It is an observed fact that there is more air present in a mechanically filled kier than in a hand-filled kier.

One method of kier boiling is to put the cloth into the kier, go through the ritual of covering, add the liquor, start circulation, put on the lid, turn on the steam, and hope for the best.

I have seen kiers started up and within 30 min. there has been 10 lb./sq.in. pressure on the gauge. It is obvious that a few tons of cloth and over 1,000 gallons of water cannot attain a temperature corresponding to this pressure of steam (viz. 240°F.) in anything like that short space of time. The worst case I ever saw was at a paper works, where they got 60 lb. pressure (supposedly 307°F.) in less than 10 min.

It is not infrequent to find kiers boiling at 20–30 lb. pressure and the circulating liquor with a temperature below the normal boiling point of water. Cloth boiled under such conditions falls far short of good practice, and will require a much more severe chemicking treatment than a well boiled cloth.

It is possible by efficient boiling with a lime boil, sour, and soda ash boil to get grey cotton to a very good colour. By doing this the cost for chemicking a ton of cloth can be reckoned in pence instead of in shillings. The simple fact is that the chemical cost is no higher when boiling is done correctly, and it can be much less. The cost

for steam is bound to be slightly higher, because in the one case the cloth is "stewed" and in the other it is "boiled". It is axiomatic that kier boiling is the foundation of good bleaching.

What are the conditions necessary to obtain the greatest efficiency from a kier boil ? After more than twenty years' close study of the subject, coupled with 2,000–3,000 fluidity control tests per annum, I have proved that seven conditions are necessary—

(1)   Correct quantity of cloth per kier
(2)   Correct filling of the kier
(3)   Correct rate of circulation
(4)   Correct quantity of liquor to cloth
(5)   Correct steam pressure in sufficient volume
(6)   Thermometers fitted to kiers
(7)   Insulation of kiers by good lagging.

CONDITION NO. 1

The kier must not be overloaded with cloth. This is a very common fault.

It has been stated that the nominal capacity of a vertical kier appears to be based on the assumption that each cubic foot of the cylindrical portion will hold 16 lb. of cloth when plaited by hand in the wet state. It has also been said that a space of 12–18 in. below the base of the dome should be left free. Under these conditions, with a load of wet, hand-plaited cloth, 80–85% of the rated load can be accommodated; and with mechanically plaited cloth this corresponds to roughly 70–75% of the rated loading.

I am not in agreement with this rate of loading. I have found in practice that perfect results are obtained by putting 10 lb. of cloth per cubic foot, plaited either by hand or by mechanical means. This is equivalent to 62% of the rated loading assumption, and within narrow limits is the quantity to which I adhere. I am aware that this will conflict with many opinions, and no doubt I shall be accused of propounding a theory that is going to reduce output. My views are that 20 cwt. of cloth boiled to perfection is better than 25 cwt. done any old how. Quality is better than quantity, and there are more ways than one of obtaining maximum production.

CONDITION NO. 2

The filling of a kier has a very great bearing on the efficiency of a kier boil. In a hand-filled kier the length of the "plaits" should be about 22 in., and the cloth should be uniformly packed by slow continual movement. Allowing the cloth to fall in small heaps and treading down tight should be avoided. Long plaits are a mistake. They do not allow free movement of cloth, and further, they are more liable to lose position and catch underneath other cloth, thus preventing ease of withdrawal after the boil. The cloth should be plaited in flat layers until near the finish of the filling, when it should be slightly raised in the centre. An up-turned saucer shape finish is better than a saucer

shape finish, as this allows the circulating liquor to flow over the whole of the cloth instead of tending to gather in the centre.

With mechanical filling it is a matter of adjustment of the throw to get the desired result. One good feature of mechanical filling is that there is no chance of the kier being filled part way with a vent hole to ease circulation. This is known practice and is sheer nonsense. By such devices the bulk of the circulating liquor travels one way, with the result that the majority of cloth gets stewed and not boiled. Mechanical filling giving peak formation, so that one can almost see the grids when all the cloth is in, is just as ridiculous.

When the kier is filled, there is no real need to cover the cloth. A string may be attached to the end of the top piece, so that it is easy to get hold of the cloth after the boil. A few bars of iron do no harm, and they do prevent distortion of the top layers of cloth when flooding up at the end of the boil. The solemn ritual of covering the top of the cloth with hessian pack sheet, baulks of timber, massive bars of iron, iron grids, and even iron chains, etc. is not necessary.

CONDITION NO. 3

The rate of circulation must not exceed the rate of percolation. It is difficult to assess accurately "rate of circulation", as the "rate of percolation" will vary according to counts of yarn, threads per inch, and weight per square yard of fabric. For average working a rate of circulation of 120 gal./min. is suitable, but for fine cloths, such as typewriter ribbon fabric, 80 gal./min. is about correct.

With a centrifugal pump the rate of circulation can be reduced by throttling back with a cone placed inside the circulating pipe on the delivery side of the pump. One cannot throttle back on the suction side of a centrifugal pump. It is important where this restriction is placed. It can be fitted immediately on the delivery side of the pump itself, or alternatively at the top of the circulating pipe.

Should the kier be heated by direct steam, it is essential that a pressure gauge reading should be taken of the circulating pipe under working conditions, because the pressure of the steam supply must be at least 15 lb./sq.in. greater than the circulating pipe pressure, the reason being that, should the pressure in the pipe be around 20 lb. and it is intended to use back pressure steam at 25 lb., in effect an attempt is being made to boil a kier with only 5 lb. effective pressure. This is too small a difference, with the result that it would take far too long to heat the kier.

The circulating pipe from the top of the pump to the top of the kier must not be too large in diameter when heating with direct steam. A 3-in. pipe is sufficient, while a 4-in. pipe is definitely too large. Comparative trials have been made, and in the larger pipe the steam and the circulating liquor can travel side by side instead of intimately mixing.

It must be remembered that a moving column of liquid is being heated and the heat must be absorbed before it is discharged from the pipe on to the cloth. Kiers with 4-in. pipes, which would not respond to the method of boiling to be described, would do so when changed to 3-in. pipes.

Care must be taken to see that the circulating liquor is discharged equally over the top of the cloth; if a ring spray is used, then the holes must be kept clean and free from stoppages, otherwise a segment may not get its quota of circulation and heat. Uniform heating is very important, and regular observation of this factor is necessary.

CONDITION NO. 4

The quantity of liquor used is proportional to the amount of cloth. This is rather difficult to express in terms of gallons, as the wetness of the ingoing cloth has a direct bearing on this factor; and again, the space under the grids is variable and will upset stated volumes. For 3 tons of cloth approx 700 gal. of liquor is necessary above the grids. Thus if x gal. is required to fill the base of the kier to the grid, then $(700 + x)$ gal. is the total required. Alternatively, the water or liquor can be added until it is just visible.

CONDITION NO. 5

The temperature of the steam used for heating the circulating liquor must not be too high.

The lay-out of steam supply to kiers often leaves much to be desired. The main should be large enough to be able to supply full steam, at all times, to all the "take-off" pipes.

The steam pressure in the main should be constant and of sufficient volume. A recording pressure and temperature gauge near to the first "take-off" is an excellent policeman and gives an accurate record, but this does not record volume.

The steam valves should be of the best type possible, and renewable-seating valves are recommended. A small by-pass valve round the steam valve to the kier is an excellent refinement, and makes for ease of operational control at or near the boil.

A steam pressure of 25–30 lb./sq.in. (261–274°F.) is satisfactory providing that there is sufficient volume, and it is enough to take a kier up to 5–10 lb./sq.in. pressure if the circulating pipe pressure is low. The steam should be "dry steam", which calls for close attention to water levels in the main boilers; "wet steam" will cause too great an amount of condensate, which affects the liquor : goods ratio.

The diaphragm of any reducing valve should be periodically renewed, and the recording instrument usually reveals when attention is required.

Many kiers are fitted with multitubular heaters and, when this is the case, the steam traps should be robust and capable of carrying away immediately all the condensate produced. It is also advantageous to insert a by-pass valve before the steam trap to ensure a clear passage for the condensate. An argument in favour of multitubular heaters is that they avoid carrying dirt and oil from the steam on to the cloth; yet one will find this same alleged dirty steam being used with open-ended pipes for boiling up starch for finishing, for dye jigs, heating up kier liquors, heating merceriser washes, etc. The argument is not sound in fact. Multitubular heaters, particularly for lime boiling, tend to lose their efficiency through deposits on the walls of the tubes.

My own preference is for direct steam heating, when such efficiency losses are eliminated, and for steam at 25–30 lb. pressure (261–274°F.).

When 50–60 lb. pressure (298–301°F.) is used, the difference in temperature between the steam and the circulating liquor is so great at the start of a boil that the heat in the steam is not absorbed by the circulating liquor before it is discharged into the kier. A large amount of available heat is thereby wasted, and it must be realised that free steam in the top of the kier can cause local overheating with consequent tendering of the top pieces.

The critical period where chemical damage occurs in a caustic alkali boil is above 190°F., so that the time taken from the start of a boil to attain this temperature is not critical, but the faster this can be achieved the better.

It is essential that the time taken to come to the boil after 190°F. is reached should be as short as possible. This is very important. A steam pressure of 50–60 lb. will "cut through" the liquor at this critical stage, when it becomes necessary to ease off the steam supply. The operative in charge has difficulty in regulating the steam to the correct amount necessary to obtain satisfaction, and it is at this stage that a by-pass valve becomes a valuable piece of equipment. With 25–30 lb. pressure steam, such adjustments are greatly simplified.

CONDITION NO. 6

Thermometers should be fitted to kiers to enable the temperature of the circulating liquor to be taken. Recording thermometers are ideal, and a double-pen type, whereby the temperature of the liquor at the bottom of the kier and that of the liquor at the top of the kier can be seen at any time during a boil, is well suited to the purpose.

One point at which to take temperature readings of the circulating liquor is in the pipe leading from the base of the kier to the pump. A second is in the pipe, near to where it discharges into the top of the kier. If only one thermometer is fitted, it should be placed in the top position, as the base temperature can be read by turning off the steam and allowing sufficient time to elapse for the cooler liquor to bring down the temperature of the pipeline, etc. before observation.

Thermometers in mercury cups give some indication of the working temperature of a kier, but are not sufficiently flexible for good work. The thermometers are best inserted into the stream of circulating liquor itself.

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CONDITION NO. 7

The kier should be well insulated by good lagging to prevent heat losses by radiation.

*   *   *

With these seven conditions fulfilled, we are now all set to boil a kier. The cloth which has been steeped, and allowed to lie overnight, is plaited down in the kier according to individual arrangements. The kier liquor is now added. This is done preferably from the bottom, so that some air will be removed by upward displacement. Where this cannot be done, arrange to fill up to the grids with liquor before putting in the cloth, in the case of hand plaiting. After all the cloth has been plaited down, add the remainder of the liquor from the top. In this way the large amount of air under the grids has not to be forced through the dense mass of cloth. In the case of mechanical plaiting, the liquor is added as required.

When the cloth and the liquor are in the kier, no matter by what system it has been filled, circulation is started and the steam valve fully opened.

The lid of the kier is left open; there is no need to leave it fully open, but it must be clear of its seating by a few inches. Continue the circulation and heating until such times as the temperature of the circulating liquor at the *bottom* of the kier reaches 190°F. The whole mass of cloth and liquor should then be at this temperature. When this stage is reached, a rest period of 10–15 min. is given, the time depending on the size of kier, when both the steam heating and the circulation are stopped.

The object of this rest period is removal of air, the presence of which not only produces cloth of high fluidity but also prevents good circulation and, in addition, the attainment of temperatures which will correspond to the working pressure of the kier. At 190°F. any air present in the kier will have increased in volume by approx. 33%.

In the rest period this swollen air will escape unhampered by the downward flow of circulating liquor, which would act as a seal and thus prevent the free escape of the air.

Imagine an air pocket in the cloth which has formed a small balloon. A descending liquid will not go through it, but will ride round it, so that the cloth immediately underneath will not get its quota of the circulation. This is a real cause of uneven scouring. During this rest period I would suggest that you look and see what is happening. The lid should be opened completely to do so, and it is usually necessary to have some means of illumination available. You will see air bubbling up profusely, and observe also that the cloth will rise up in the kier. There are no leprechauns or gremlins pushing up the cloth. It rises because of "air-lift". Should there be too much cloth present, it will rise and press on the dome of the kier and thus prevent free egress of air. The cloth must have sufficient breathing space. I know that at the end of the boil, when the lids are lifted and you look inside the kier, it would appear that you could have got a lot more cloth into the kier. It is a great temptation to load to capacity, but it is an evil which must be avoided. The air cannot be completely removed unless the cloth has freedom of movement at this stage.

After the rest period the lid is placed in position, the air tap left fully open, circulation restarted, and the steam turned on. When the temperature of the circulating liquor at the bottom of the kier reaches 200°F., a second rest period is given for about 5 min. By inserting a thin iron rod through the air tap, just before stopping for the second time and marking it with chalk at the level of the air tap, it can be seen whether the cloth rises when steam and circulation are stopped. If it does rise, air is still present. Measure the rise. When circulation is restarted after this second rest period, the rod will fall. Measure the fall, and it should be greater than any rise. Remove the rod. Turn on the steam and continue the boil. The air tap is still left fully open.

Proceed with the boil until the temperature of the circulating liquor at the bottom of the kier approaches 210°F., when a third rest period may be given for 5 min. It is not always necessary to have three periods of rest for the elimination of air, but only experience of the extent of the "fall of the cloth" which has taken place can be a guide on this point. If the third rest period is given, repeat the measurement of any rise and fall by the rod technique: there should be little or no rise and fall at this stage.

When circulation is restarted, the steam will have to be checked back a little. The air tap is still left fully open. It may, however, be slightly closed when the temperature of the circulating liquor reaches 215°F. at the top of the kier; it must not be closed until the temperature of the circulating liquor at the top of the kier has reached 220°F. This ensures that all the air between the top of the cloth and the top of the kier has been eliminated.

From the start of the boil to the closing of the air tap will take approx. 4 hr. for a 4-ton kier.

The steam is checked, as necessary, until the desired temperature is reached. Do not try to build up pressure rapidly. For a 10-lb. pressure boil, very little "set" on the steam valve will maintain a temperature of 240°F. Both pens of a double recording thermometer will now be travelling on the same line.

It will be found that by this method of boiling kiers the temperature of the circulating liquor will differ by ±1°F. from that of steam at the pressure at which the kier is boiling.

Boiling is carried on for the requisite period. Let us assume this is 10 hr. at 10 lb. pressure.

With this method of boiling in well lagged kiers, only about 2 lb. pressure will be lost per hour when the steam is turned off. That being the case, the steam can be safely turned off 2–3 hr. before the end of the boil, so that the kier can lose pressure gradually by working itself back. There will still be 4–5 lb. pressure (228°F.) left at the end. When

the end of the boil has been reached, the steam is turned off, unless this has already been done on the working-back system, and circulation is stopped.

To release the pressure in the kier, open the air tap slightly. Too rapid release of pressure causes a terrific ear-splitting noise. In addition to opening the air tap, the weight of the safety valve can be eased to get additional relief. This keeps the safety valves in working order.

The pressure must be completely released before opening the kier. Do not lift the lid or lids until it is perfectly safe to do so, and have arrangements made beforehand whereby the kier can be flooded with cold water. A plentiful supply of water is necessary. Flood the cloth with water, and when it is awash open the let-off valve so as to run the liquor away at the same rate as the flooding water is entering; a little practice puts you wise as to the details. Test the temperature of the let-off liquor, and when it has fallen to 150°F. or lower you can do one of two things—

(1) Shut the let-off valve and stop the flood water. The kier can then be drained at any time desired.

(2) Stop the flood water, fully open the let-off valve, and allow the kier to drain.

Sufficient drainage time should be allowed before drawing out the cloth. A boil finishing on Saturday morning can be flooded up and left over the weekend; it will have cooled down sufficiently before Monday.

Many kiers are "blown down" while still under pressure, but I do not favour this practice, as air is bound to get into the very hot cloth, which still contains caustic alkali, and this is not desirable.

A kier boiled under the conditions described will conform to the highest standards of chemical testing, and also the uniformity of scouring will leave nothing to be desired.

It is my experience that there is no need to boil cloth at high pressures such as 20–30 lb. If cloth is boiled at 10 lb. pressure and the temperature corresponding to that pressure, it is perfectly satisfactory.

This description of kier boiling has so far had reference to high-pressure boiling, but the same technique is equally applicable to low-pressure boiling. There are many bleachworks which operate only a low-pressure boiling system and produce a first-class result. The ratio of goods to size of kier, the filling, and the ratio of water to cloth are just the same. The periods of rest during the preliminary part of the boil are just as necessary to get rid of the imprisoned air.

Low-pressure kiers fitted with puffer-pipe circulation will require the thermometer fitting through the side, or base, of the kier just under the grids. This gives temperature readings after the liquor has passed through the cloth. After a low-pressure kier boil, it is still desirable to cool the cloth by flooding with cold water.

SODA-ASH KIER BOILING

Chemical damage cannot occur in cloth during boiling with sodium carbonate solution, but it is just as essential to follow the same routine of boiling. By removal of air a more uniform circulation and thereby a more level scouring are achieved. The cleaner the cloth after boiling the less bleaching agent is required, and this will remain stable for a longer period than on a less satisfactory scoured material. There is no real need to cool the cloth prior to draining and removing it from the kier.

CAUSTIC-SODA KIER BOILING

The above method of boiling kiers, if strictly carried out, eliminates the danger of tendering by a caustic soda boil. After a caustic soda boil I advocate flooding with water to get the temperature of the cloth down and then draining the kier.

When drained, run into the kier a warm solution of sodium bicarbonate (about 56 lb. per 1000 gal. for a 3-ton kier) and circulate this for 30 min. This will convert a good deal of the weak caustic soda present into sodium carbonate. Run off this wash liquor, allowing time for drainage, and the cloth is ready for drawing out. This bicarbonate wash reduces the causticity of the cloth, and it is less liable to "slip" in the washing machines.

If bicarbonate is not available, a weak warm sodium carbonate wash is better than nothing to help in the same direction.

*   *   *

When the cloth has been taken out of a kier, it is good practice to wash the grids and the base of the kier with plenty of water to get rid of any extraneous matter which may be present. This will keep down the incidence of filtered-on stains.

It is worthwhile recording outstanding occurrences during these investigations into kier boiling—

(1) A kier with 30 lb. pressure on the gauge and the temperature of the circulating liquor 208°F. This is 66°F. too low.

(2) A kier with 20 lb. pressure on the gauge that had steam blowing from a defective joint on the suction side of the pump. This could only have happened because there was no liquor in the base of the kier for the pump to circulate.

(3) A kier with a circulating pump speed of 320 gal./min. This is an impossible feat with a kier properly filled with cloth.

(4) On starting up a pair of high-pressure kiers which had been out of commission for some time, a curious event took place. The kiers were of 3 tons capacity, of double-manhole type with vertical grating division, pump circulation, and direct steam heating. The pump was belt-driven from a line-shaft driven by a small steam engine. No. 1 kier was used for a lime boil and No. 2 kier for a soda ash boil. After five days it was found that the soda ash liquor in No. 2 kier would not circulate—the pump just refused to lift the liquor. Consultation with the works engineer brought to light that he had been told of such a phenomenon by his father. The cure was to reverse the kier

operations, make No. 2 kier the lime boil and No. 1 the soda ash boil. The changeover was made and worked perfectly, nothing being done to the pump. Every three days operations were reversed, and no further trouble was encountered.

* * *

In the general arrangement of kiers and in their operation there are a few things which should not be tolerated—

Never allow a pump to operate when a kier is filled with cloth with no liquor present, as this will suck the cloth tight on the grids and make subsequent circulation difficult. Too high a rate of circulation can bring about this circumstance even with liquor present, as the liquor may all be deposited on top of the cloth, and this can lead to broken grids.

A further contributory cause of broken grids is overfilling the kier with cloth. The air expansion during the boil lifts the cloth hard up against the dome, and if there is not sufficient relief, the pressure is exerted downwards and the grids may not carry the strain.

It has been practice to put crossed chains over the cloth to prevent it from rising, but here, again, undue pressure is exerted, and I have seen broken grids and broken chains because of this confinement.

The "turning over" of cloth in a kier is due to irregular "air-lift", and cannot happen if the air is expelled as indicated.

Do not put the exhaust from a steam pump into the circulating liquor of a kier which has to operate under pressure, for this obviously causes back-pressure and thus commences a vicious circle.

Do not allow pump glands to draw air along the spindle.

Do not put a vent pipe against the side of the kier, allegedly put there to equalise pressure top and bottom, for it can act as a by-pass for the circulating liquor.

Never increase the height of the grids of a kier. This has been tried on several occasions with the object of giving a greater reserve of liquor for the pump or puffer pipe. If the grids are raised, there is liable to be badly stained cloth at the bottom of the kier. Wanting to raise the grids indicates that the rate of percolation is too slow for the rate of circulation. Under ideal conditions there would be no need for grids at all, but this would be difficult to achieve in practice, and is never likely to be attained.

That is my experience of boiling kiers. The method will give cloth perfectly and uniformly scoured which will show textbook fluidities, and the circulating liquor will be within $\pm 1°$F. of the temperature of steam at the working pressure of the kier.

The method has stood the test of time for over twenty years, and surely that is a long enough trial. I do not ask you to believe it, but merely to try it for yourselves. To anyone sufficiently interested and disposed to make trials, might I suggest that you start by fitting a thermometer to one of your kiers and operate your present system for a week, taking records of times, temperatures, and fluidities?

You may consider that three fluidity tests per kier boil is too much of a good thing. May I stress that until you have gathered sufficient information you should do it? You can, at a later stage, reduce this to top and bottom only, but that is the absolute minimum.

A bleachworks without fluidity control of its process is like a ship without a compass.

When you have got some records of your present system, make any adjustments and modifications necessary to bring the same kier into line with my suggestions, and then compare the two sets of results.

I am confident that you will be pleased with the result and be only too anxious to fit up your remaining kiers.

It may seem fatuous for me to stress this point, but you must have all conditions fulfilled. Each and every one has a direct bearing on the result, and therefore it is a case of all or nothing.

In conclusion, I must state that even in the best regulated of processes there can be the occasional failure to obtain ideal fluidities. The human element is not infallible, but when you do fall from grace an immediate investigation must be made. There is always a definite cause for any failure; therefore checking up on steam and kier charts is a natural starting point for such an investigation. If the answer is not to be found there, you may find that some overzealous person has put through some hurried goods without an overnight steep, or has overloaded a kier to hold a particular unit of cloth.

I trust that this paper has stimulated your interest in kier boiling, so that in future you will have a respect for, and a more sympathetic attitude towards, those who toil among the kiers.

May I suggest that you pay a weekly bonus, based on a fluidity of 3·43 or lower, for each unit of cloth given a caustic alkali boil. This should be given to the person responsible for filling the kier and also to the person responsible for boiling the kier. The foreman bleacher should also receive a bonus for maintaining the low fluidity. Such incentives pay handsome dividends and encourage an interest in what, to some, may appear a sterile occupation, but which is actually the lifeblood of the textile trade.

* * *

Finally, I wish to thank the Directors of Messrs. Lumsden & Mackenzie Ltd. for permission to put this paper before you.

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Discussion

Mr. A. S. FERN: On p. 835 the author states that a bicarbonate wash reduces the causticity of the cloth, which is then less liable to slip in the washing machine. Is there any explanation of this phenomenon? For example, is the coefficient of friction between cellulose and the materials normally used in washing-off equipment less in caustic soda solution than in sodium bicarbonate solution?

Mr. GARRETT: The main reason why slip occurs when cloth from a caustic soda boil is washed in a washing machine is the fact that it is difficult to wash cloth free from caustic soda by cold-water washing. Hot-water washing is more effective, but is not practicable. A contributory factor is the construction of the bowls: wood and wood, one wood–one roped, one wood–one rubber, etc. The pressure on the bowls, the tightness of the cloth in the washing machine, the distance the cloth is pulled, and the ease of path of travel from the kier also are important. When washed from a soda ash boil each strand diminishes rapidly in alkali content from entering to exit, and the final strand is usually free from alkali; but from a caustic soda boil it is more difficult to get the cloth free from alkali.

Analogous to this is mercerising practice: many mercerising plants operate a souring box after the cloth leaves the clips to ensure freedom from caustic soda before the cloth is plaited down. If, instead of acid, a sodium bicarbonate box is used, the result is equally satisfactory, and this method is claimed to be less costly.

A simple laboratory experiment will prove the fact that a bicarbonate treatment facilitates washing caustic soda out of cloth by either hot or cold water.

Mr. E. MOSS: There are several factors which have not been mentioned but which have a great effect on the efficiency of kier boiling. Sufficient alkali must be used initially to ensure the presence of free alkali in the liquor at the end of the boil. In the caustic boil the final concentration in the liquor should be not less than 0·3%. In the lime boil an excess of lime should be present at the end. The addition of emulsifying agents in both caustic and lime boils also improves the quality and the rate of scouring considerably.

Mr. GARRETT: The paper was designed to cover how to fill, boil, and empty a kier, and suggestions for concentrations of kier liquors were omitted for the reason that each works has its own ideas on this point. It was considered outside the scope of the paper to go into this important question. There is no doubt that there must be sufficient alkali at all times and that additives can be useful. Much work has been published on these lines.

Mr. MOSS: How has the author arrived at the exact fluidity figure of 3·43 quoted in the last paragraph of the paper as the basis for a bonus payment?

Mr. GARRETT: The exact fluidity figure of 3·43 quoted as a basis for bonus payment dates back to the days of viscosity. The aim of the directorate was a viscosity of 2·0 on the fully bleached cloth, and it was considered that a viscosity of 2·5 (fluidity 3·43) on the fully boiled cloth was ample margin for the foreman bleacher to whiten his cloth to the desired standard.

Mr. E. BUTTERWORTH: I should like to take this opportunity of paying a tribute to the originators of this most important viscosity test. The paper by Gibson, Spencer, and Macall in 1919, on the viscosity of cellulose in cuprammonium [1], marked the beginning of a new era in cellulose technology, and while later investigations have been responsible for much of the refinement and interpretation of the test and its results, yet I think sufficient recognition has not always been accorded to its original sponsors.

I would like to ask Mr. Garrett if he has had experience of an effect first noticed by T. Barritt in some of the early work on the production of cellulose for explosives. When cotton was kier-boiled in sodium hydroxide, the viscosity of the resulting cellulose was markedly lower when the boiling was conducted with a continuous slight blow of steam than with a boil under identical conditions, and at the same nominal gauge pressure, where no steam escaped (the normal method of kiering).

Mr. GARRETT: As far as I am aware, no adequate explanation of this effect has yet been given.

Mr. H. A. TURNER: It seems to me that, as long as kier boiling is the most convenient method to adopt for thorough alkali purification of natural cellulosic fibres, the procedures and the advice of Mr. Garrett should be followed as thoroughly sound. Nevertheless, if the restrictions imposed by the existing types of plant are disregarded and the question is looked at from the beginning, the assertion that continuous processes will never supersede kiering for thorough purification seems to be going rather too far. Is there any evidence that the actual process of extraction of impurities from cotton, say, by alkali is essentially a slow one, if the fullest possible access of the reagent is achieved? Does it take hot caustic soda solution hours to modify the impurities sufficiently for them to be extracted, or is it only the low liquor ratio and slow rate of liquor displacement which make normal kier boiling a relatively slow process. Has Mr. Garrett any evidence which could bear on this aspect of the problem?

Mr. GARRETT: So far as I am aware, there is no continuous bleaching process that gives the degree of purification of cellulose that kiering can achieve.

Over 1·0% ether-extractable matter has recently been found in cotton continuously bleached on the Continent, showing absence of scouring, with absorbency probably obtained by means of synthetic detergents. Even solvent extraction to remove natural and added fats and waxes does not make either cotton or linen fabrics easier to bleach. The final bleached fabric has a very low grease content, but the cost of achieving this is very

considerable, and equally good results can be obtained by efficient kiering.

There appears to be ample practical evidence that the removal of impurities from cotton by hot caustic soda is a slow process, as otherwise greater liquor ratios at higher concentrations would have been in use before now.

Dr. P. W. CUNLIFFE: In general support of the author, we find that in yarn bleaching a fluidity not exceeding 5 can be, and is, regularly attained.

Some time ago I sent a grey sheet to a laundry for washing only. It came back a sparkling white, and I found that it had a fluidity of 20. On enquiry at the laundry I found that, not only had it been bleached during the day, but, being dissatisfied with the colour, the operative had left it overnight in a hypochlorite solution containing 3–4 g. chlorine per litre. Clearly, there is scope for an extension of Mr. Garrett's campaign to other fields!

Mr. GARRETT: This illustrates very clearly what is required. Until a fluidity standard for processed fabrics becomes established, the laundry industry has a "back door"; they are well aware of the present standard. Once a standard becomes a reality, then it will be imperative for laundries to improve their methods. Likewise, the makers of dangerous washing compounds will have to issue due warning and precise instructions of use to the housewife.

Dr. C. A. MUHR: Kier boiling is a dangerous process for linen. That is, perhaps, the reason why the fluidity test was introduced. The best result in linen bleaching is obtained by giving a light boil with sodium carbonate and then bleaching with chlorite (5–7 g./litre). With this process there is practically no loss in tensile strength. With kier boiling the loss is about 10%. Chlorite bleaching is more expensive, but for a high-quality fabric like linen it is the answer to our difficulties.

Mr. GARRETT: I cannot agree that kier boiling of linen yarn is a dangerous process. Enquiries have shown that linen yarn should have a greater tensile strength after kier boiling than before. It would appear from the example quoted that the method of bleaching as well as any doubtful boiling must have played some part in the 10% loss of tensile strength. It is noteworthy that the improvement was brought about by the use of sodium chlorite.

Mr. R. J. G. REID: According to the paper the major danger of high fluidity developing in the kier is the presence of air. What is the most efficient method of eliminating air, and what importance does the author attach to the size of the air outlet?

Mr. GARRETT: The elimination of air has been fully described in the paper. The outlet should be 2–3 in. in diameter. A small air-tap is not desirable, but whatever the size the time at which it is closed is most important.

Mr. REID: Large quantities of linen and cotton cloth are lime-boiled and caustic-boiled daily following singeing and impregnation, and then piled into kiers. Why does Mr. Garrett not look upon this as a safe procedure?

Mr. GARRETT: When fabrics are run through water in the mangle of a singeing machine, most of the liquid can be brushed off by hand. It takes time for the liquid to seep into the cloth, so that "lying time" is necessary for the cloth to be thoroughly damped. This is a case where it would be wise to try both methods and judge for oneself which is the better way.

Mr. REID: What fluidity would Mr. Garrett set for an efficiently lime-boiled linen cloth?

Mr. GARRETT: The fluidity of an efficiently lime-boiled linen cloth after souring and soda ash boiling should be in the region of 2·0–2·5.

Mr. H. WILSON: Does Mr. Garrett support, in the interests of avoiding the danger of degradation or tendering, the introduction of wash waters to a kier whilst some pressure is still retained from the kier-boiling operation? The following would be the detailed procedure— Shut down steam, release pressure gradually to, say 5 lb./sq.in., shut off pressure-release valve, introduce wash waters with continuous circulation, and then proceed to release kier liquors, maintaining a quicker rate of intake of wash water than rate of release of kier liquors. Is this procedure not a safeguard against the possibility of introduction of air prematurely, and conducive to yielding an excellent fluidity figure in subsequent control tests?

Mr. GARRETT: The introduction of wash waters to a kier under slight pressure would be difficult to control in practice. The wash waters would have to be at a pressure greater than the kier pressure, and a special inlet valve would have to be provided. The existing pipe-lines being in use for circulation, there would have to be a special discharge valve. An interesting suggestion, but operationally difficult.

Dr. T. E. ELLISON: It will generally be agreed that the degradation of cellulose in the bleaching of cotton and linen textiles should be kept to a minimum. In appearing to suggest, by his reference to ships without rudders, that Irish linen bleachers are at fault in not using the fluidity test, Mr. Garrett does less than justice to the trade and to its scientific advisers. The important facts of the matter would seem to be as follows. The fluidity test using a capillary tube viscometer, as described by Clibbens and Geake in 1928, was not at first easily applicable to linen at any stage below a full bleach, owing to the insolubility in cuprammonium of parts of the linen cellulose complex. In these circumstances, it was a notable achievement of the Linen Industry Research Association that, as early as April 1929, gave to linen bleachers the alternative method of

solubility number [2]. That there was no misunderstanding of the position is shown by the following quotation [3]—

> The cuprammonium viscosity method is considerably more sensitive and reliable for indicating the initial stages of attack. . . . for general purposes, however, particularly with linen goods, the solubility number method is eminently suitable and decidedly simpler.

By the systematic application of solubility number, in conjunction with a steadily growing understanding of the science of bleaching, the general level of bleaching in the Irish linen trade, especially in yarn bleaching, has much improved, so much so that the time is perhaps fast approaching when fluidity will have to be used for plant control in place of the less sensitive solubility estimation. To imply, however, if that was the intention, that linen bleachers in this country have been either remiss or misled in not adopting the fluidity test earlier would be entirely to misread the history of the past twenty-five years.

Mr. GARRETT: It would appear that the context of my remarks has been entirely misunderstood. I called attention to the state of things as they exist today in the linen trade, both British and Continental, not in any sense of criticism but with suggestion for improvement. My plea was for the British Standards Institution to make the fluidity test an official method of testing for the degradation of linen, and I made no mention of the solubility number test. Now that the matter has been raised in this question, may I point out that those who wish to do so may use the solubility number test? And by the same token, those who prefer the fluidity test (and their number is growing in the light of experience) can use the test of their choice. Thus we have two methods and we have freedom of selection.

My plea still stands, and as the fluidity test is a fundamental method, which the solubility number test is not, there is no valid reason why the fluidity test should be denied official recognition by the B.S.I. as a method of determining the degradation of linen.

Dr. G. SCHWEN: In Germany a reducing agent, e.g. Rongalite C, is often used to remove air from the kier.

Mr. GARRETT: Never having used anti-oxidants for this purpose, I cannot quote from experience, but I would doubt the uniformity of action throughout the mass. They could not deal with pockets of air, which can arise from time to time. It could also be a costly enterprise.

Mr. H. À BRASSARD[*]: It is undoubtedly true that those of my era kier-boiled millions of yards of fabrics and yarns long before the First World War and achieved remarkably good results, though litmus, Congo Red, and Phenolphthalein were their only indicators. But it is fortunate that the author has so thoroughly investigated the technique.

Although I submit that boiling a fibre for long periods, whether under pressure or not, can hardly be good for it, I do agree that a proper kier boil is an essential basis for further processing. It is surprising, therefore, that the author brought no evidence to show that boils of 8, 10, 12, or more hours were essential.

Mr. GARRETT[*]: My paper was designed to give the fundamentals of kier boiling, and purposely avoided entering into the field of bleaching processes. There is an optimum strength of liquor whether lime, caustic soda, or soda ash is used; there is also an optimum time of boiling, which depends upon the concentration of alkali and the temperature at which it is used. The bleaching process in a works is geared to the result required on a particular type of cloth, so that concentration of solution, time of boiling, etc. are individual requirements.

Mr. À BRASSARD[*]: I was surprised that the author did not say whether the addition of appropriate auxiliaries was useful or not. In my own fairly wide experience I have no doubt whatever that they are helpful. Surely they assist wetting-out quickly, and therefore freeing fibres from air, apart from the other important part they play.

Mr. GARRETT[*]: Appropriate auxiliaries can be and are of use in certain circumstances, but they must not be regarded as necessities.

Mr. À BRASSARD[*]: Does Mr. Garrett prefer a caustic soda to a soda ash kier, and if so why?

Mr. GARRETT[*]: My preference as a bleaching treatment is the full lime bleach, because a cotton fabric virtually resolved to pure cellulose and having a grease content well below 0·1% can be obtained with monotonous regularity.

Mr. R. W. SPEIRS[*]: After a caustic soda boil, Mr. Garrett recommends immediately flooding the kier with cold water and then draining off. Is this not likely to lead to reprecipitation of impurities on the material? The impurities have been digested into a colloidal solution, and there might be separation on sudden cooling.

Mr. GARRETT[*]: In practice there is no evidence of trouble arising from flooding a kier of cloth with cold water after a caustic soda boil. This flooding is followed by circulation of warm sodium bicarbonate or carbonate, and this is evidently sufficient to correct any tendency for separation. You will note that I have stated on p. 835 that there is no real need to cool the cloth prior to draining and removing the cloth from the kier after a soda ash boil.

References

[1] Gibson, Spencer, and Macall, J.C.S., 117, 473 (1920).

[2] Kinkead, R. W., and Nodder, C. R., L.I.R.A. Memoir No. 58.

[3] Nodder, C. R., J. Textile Inst., 22, T 423 (1931).

* Communicated

Recent Progress in the Dyeing of Terylene Polyester Fibre

A. S. FERN and H. R. HADFIELD

The first part of this paper summarises existing knowledge of the dyeing of polyester fibres, and indicates how the main developments in dye application have taken place. The second part describes mainly unpublished work on Terylene polyester fibre concerned with the application of azoic dyes and the dyeing of blends of Terylene with wool.

A— Introduction

This is an opportune moment to review the dyeing of polyester fibres, since the production of Terylene* polyester fibre is in the transition stage between the pilot scale and the bulk scale, and because no paper has appeared in the *Journal* on the general dyeing properties of this type of fibre since that by Waters [1] in 1950. Many British dyers have now had an opportunity of undertaking trials on the forms of Terylene in which they are interested, and it is possible, from these trials and from laboratory work such as that described below, to draw some conclusions about what is possible and what is impossible with 100% Terylene and Terylene mixture materials at the present time, and what developments are most desirable in the immediate future. It is impossible in a survey such as this to ignore the published contributions made on Dacron† in the U.S.A., and the most important have been mentioned. The experimental work described below, however, was done on Terylene polyester fibre only.

Since Waters [1] showed that Terylene had a capacity for disperse dyes which was not reflected by the small amount of dye taken up at 100°c. in a practical dyeing time, the main problem has been to speed up the rate of diffusion of these dyes into the fibre. The earliest recommendations for dyeing Terylene in conventional equipment involved the disperse dyes of smaller molecular size, which diffuse relatively quickly into Terylene, and which give dyeings of at least medium depth after dyeing at 100°c. for about 90 min. Examples of these dyes are—

Dispersol Fast Yellow G
Dispersol Fast Orange G
Duranol Red GN
Duranol Red 2B
Duranol Violet 2R
Duranol Blue GN

In addition, several scarlet and red azoic combinations were available which were built up from comparatively small and quickly diffusing units by a diazotisation and coupling process on the fibre.

At this stage it was, of course, known that dyes possessing high solubility in water were of no practical value for dyeing Terylene. From this observation a most valuable aftertreatment for the dyed fibre was devised. When Terylene was

dyed in medium or heavy depths with disperse or azoic dyes, particles of dye or of intermediates were often held firmly to the fibre surface even after a normal scouring process. Treatment in a hot reducing solution of sodium hydroxide, sodium hydrosulphite, and Lissolamine A (ICI) efficiently removed surface dye without appreciably affecting dye inside the fibre and gave a dyeing of greatly improved brightness and rubbing and wet fastness. This process was called "reduction–clearing", and is still recommended for all medium–heavy dyeings on Terylene if it is suspected that surface dye will be detrimental to the final fastness.

The quickly diffusing disperse dyes were very valuable in the early days of Terylene development for dyeing typical mode shades on staple half-hose and pale colours on light-weight Terylene continuous-filament fabrics, which were two of the major textile outlets for the fibre at the time. They possessed one serious drawback, however, namely their readiness to diffuse out of the fibre under the influence of heat, and to a lesser extent of wet treatments. It was soon realised that they were unsuitable, for this reason alone, for many of the uses to which the Terylene fibre might reasonably be put. Similarly the azoic dyes, although not being affected much by heat themselves, usually gave volatile products (yellow or brown stains on adjacent white material) when subjected to a dry-heat sublimation test. This was considered to be due to incomplete coupling of the components or to undesirable side-reactions during diazotisation. A method of obtaining dyeings with disperse dyes of superior sublimation fastness was urgently required and this inevitably meant that techniques for speeding up slowly diffusing dyes had to be devised. The problem of possible poor sublimation fastness resulting from uncoupled azoic intermediates will be discussed later.

Two solutions to this problem were immediately available. The first was to use an assistant (or "carrier") in the dyebath which could, e.g. by swelling the fibre, increase the effective pore size of the polymer, so that dyes would diffuse in more rapidly at temperatures up to 100°c. Thus it might be possible to obtain heavy dyeings on Terylene in conventional equipment. The second was to raise the temperature above the boiling point of water at atmospheric pressure, by using a high-temperature dyeing machine. Carrier dyeing is dealt with in some detail later in this paper, and the fundamental dyeing properties of a range of

disperse dyes under high-temperature dyeing conditions have recently been described by Fern [2].

By either of these methods it became possible, not only to obtain heavy dyeings from the more quickly diffusing dyes, but to use economically a much wider range of disperse dyes having desirable fastness properties and colours. A workable range of disperse dyes having much better sublimation and wet fastness than those originally proposed was selected, and by mixing these most colours could be obtained with good light fastness [3]. This range is as follows—

> Dispersol Fast Yellow A
> Dispersol Fast Yellow GR
> Dispersol Fast Orange B
> Dispersol Fast Orange Brown RN
> Duranol Red X3B
> Duranol Brilliant Violet BR
> Duranol Blue G

A similar development was taking place in the U.S.A. This eventually gave rise, for example, to the Latyl (DuP) range. Although certain of these dyes possess comparatively poor building-up properties even in presence of a dyeing assistant or at high temperatures, most members have very high light fastness and at least moderate sublimation fastness on Dacron. Without these two new dyeing techniques, it would have been impossible to select dyes of this type for economic application to this type of fibre.

In the same way, the palette of colours obtainable from azoic combinations was augmented by the introduction of carrier and high-temperature processes. These developments, however, will be discussed in greater detail elsewhere in this paper

B— The Properties of Disperse Dyes

It has previously been explained that the initial difficulties experienced in dyeing Terylene resulted from the low rate of diffusion of dyes through Terylene compared with their diffusion through acetate rayon or nylon. An important advantage resulting from this low rate of diffusion is the high wet fastness of disperse dyes applied to Terylene compared with the other two fibres (Table I).

TABLE I
Fastness to Washing
(30 min. at 55°c. with 5 g. soap flakes per litre)

Dye (medium depth)	Type of Fibre*	Change in Colour	Staining of Adjacent Undyed Fibre†
Dispersol Fast Yellow G	A	3	3
	N	4–5	3
	T	5	5
Dispersol Fast Orange G	A	3	3
	N	4	2
	T	5	5
Duranol Red 2B	A	2	1
	N	4	2
	T	5	5
Duranol Blue GN	A	3–4	3
	N	5	3
	T	5	5

* A = Acetate rayon
 N = Nylon
 T = Terylene
† In each case the same as the fibre used for the dyeing

The rate of diffusion of disperse dyes through Terylene varies widely from dye to dye. The dyes of highest diffusion rates, e.g.—

> Dispersol Fast Orange G
> Duranol Red 2B
> Duranol Violet 2R

build up most readily to deep colours. Dyes with comparatively low diffusion rates, e.g.—

> Dispersol Fast Orange B
> Duranol Red X3B
> Duranol Brilliant Violet BR

are more difficult to build up to heavy depths, and indeed, unless a carrier, or preferably a dyeing temperature of 120°c., is used, these dyes will not build up very well. In the same way as disperse dyes are faster to wet treatments when applied to Terylene than to acetate rayon or nylon because of a lower rate of diffusion, the disperse dyes of lowest rate of diffusion through Terylene are appreciably faster to wet treatments and sublimation than those of higher rates of diffusion. An important property of dyed Terylene is the ability of the dyes used to withstand a durable pleating process when, for example, the dyed Terylene is blended with wool. One method of

TABLE II
Fastness to Steaming
(One hour at atmospheric pressure)

Dye	Type* of Dye	Change in Colour	Staining of Undyed— Terylene	Staining of Undyed— Wool
Dispersol Fast Orange G	R	4	2	2
Dispersol Fast Orange B	S	5	4	3–4
Duranol Red 2B ...	R	4	2	2
Duranol Red X3B ...	S	5	3–4	3–4
Duranol Violet 2R ...	R	4–5	2	2
Duranol Brilliant Violet BR	S	5	4–5	4–5

* R = Rapidly diffusing dye
 S = Slowly diffusing dye

durable pleating is to steam for one hour at atmospheric pressure. In Table II a comparison is made of the fastness to the pleating process of rapidly and slowly diffusing dyes.

Fastness to dry heat treatments is also an important property of dyed Terylene and must be considered in selecting dyes for hosiery yarn and yarns for coloured effect threads. In Table III a comparison has been made of the sublimation fastness of the rapidly and slowly diffusing disperse dyes.

In general it is found that the light fastness of a disperse dye is significantly higher when applied to Terylene than when applied to nylon. The difference is much more marked with azo disperse dyes than with anthraquinonoid disperse dyes. It is generally found that the light fastness of disperse dyes on acetate rayon is similar to that of the same dyes on Terylene (Table IV).

TABLE III
Dry-heat Sublimation Fastness of Disperse Dyes on Terylene
(Staining of undyed Terylene)

Dye		Type of Dye*	5 min. at 120°C.	15 sec. at 150°C.	15 sec. at 170°C.	15 sec. at 190°C.
Dispersol Fast Orange G	...	R	3	3–4	2	1
Dispersol Fast Orange B	...	S	5	5	5	4
Duranol Red 2B	... ...	R	3	3–4	2	1
Duranol Red X3B	... ...	S	5	5	5	3
Duranol Violet 2R	... ...	R	2	3	2	1
Duranol Brilliant Violet BR	...	S	5	5	5	4

* R = Rapidly diffusing dye
S = Slowly diffusing dye

TABLE IV
Daylight Fastness of Disperse Dyes on Delustred Acetate Rayon, Nylon, and Terylene

Dye (medium depth)		Acetate Rayon	Nylon	Terylene*
Dispersol Fast Yellow A	...	4–5	2–3	6–7
Dispersol Fast Orange B	...	5–6	5	6–7
Dispersol Fast Scarlet B	...	5	2–3	4
Duranol Red 2B	... ...	6	3–4	6
Duranol Red X3B	... ...	4–5	4–5	5
Duranol Violet 2R	... ...	5	4–5	5
Duranol Brilliant Violet BR		5–6	5–6	5
Duranol Blue G	... ...	4–5	5	5

* Applied at 120°C.

As is the case with the majority of dye–fibre systems the light fastness of most disperse dyes applied to Terylene decreases as the depth of dyeing is decreased. There are, however, a number of exceptions to this behaviour, where the disperse dye applied to Terylene shows decreased fastness to light as the depth of dyeing is increased. With these exceptions the fading is not usually a straight bleaching of the dyeing, but takes the form of severe change in hue (Table V) [4].

TABLE V
Unusual Effect of Depth of Dyeing on Daylight Fastness

Dye		Pale Colour	Full Colour
Duranol Orange G	...	5–6 Redder	3–4 Redder
Duranol Red GN	...	5 Yellower	3–4 Yellower
Duranol Brilliant Blue B		2 Redder	1 Redder

Carriers, also, can seriously affect the light fastness of many dyes. In general, Tumescal D (ICI) (effective agent diphenyl) has no detrimental effect, Tumescal OP (ICI) (effective agent o-phenylphenol) has a slight effect (an average reduction of 0·2 S.D.C. unit over the complete Dispersol and Duranol range), whilst Tumescal PH (ICI) (effective agent p-phenylphenol) can have a very severe effect indeed (an average reduction of 0·5 S.D.C. unit over the complete Dispersol and Duranol range).

It is now well known that fading-lamp ratings are not a reliable guide to daylight ratings for dyes applied to polyester fibres [4, 5]. Over a series of ninety dyeings the average fading-lamp rating on Terylene was 1·5 units of light fastness lower than the average assessment of daylight exposures. However, no instance has yet been encountered where the fading-lamp ratings have been higher than corresponding daylight assessments, and accelerated fading may be of some value as a guide to the minimum light fastness of a dyeing.

C— Carrier Dyeing

A large variety of organic hydrocarbons, substituted hydrocarbons, phenols, amines, acids, amides, alcohols, ketones, nitriles, esters, etc. accelerate the rate of dyeing of disperse dyes on polyester fibres at temperatures up to 100°C.[4, 6–12] and are generally referred to as "carriers" or "swelling agents". Few compounds, however, have sufficiently attractive properties to justify their commercial use. A successful carrier must be cheap, effective, unobjectionable, simple to use and remove, and without detrimental effect on the fastness properties or the fibre. No carrier is yet known which satisfies all these requirements.

Carriers now being used in the United Kingdom are based on diphenyl, o- or p-phenylphenol (2- or 4-hydroxydiphenyl), mono- or di-chlorobenzene, and mixtures of tetrahydronaphthalene with cyclohexanol. In America, benzoic acid, salicylic acid, methyl salicylate, and a mixture of methylphenylcarbinol with acetophenone are also widely recommended. More recently, Collins [12] has drawn attention to the merits of β-naphthol as a carrier for Dacron, in spite of its known toxicity.

The water- and alkali-insoluble agents like diphenyl and monochlorobenzene are added to the dyebath as aqueous emulsions or dispersions; agents like benzoic acid and o-phenylphenol can also be used in this way, but it is more usual to predissolve them with sodium hydroxide (or to use the ready-made sodium salt) and liberate the free acid or phenol at the desired rate by gradually adding a weak acid during the dyeing process.

The relative practical merits of these carriers are summarised in Table VI.

Vickerstaff [13] has described possible modes of carrier action, such as increasing the solubility of dye in water, swelling or plasticising the fibre, or forming new dye sites. He differentiates between water-soluble carriers like benzoic acid and water-insoluble carriers like diphenyl. Experimental

TABLE VI
Properties of Existing Carriers

Carrier	Efficiency on Weight Basis	Effect on Light Fastness	Possible Hazards	Smell	Ease of Removal	Level-dyeing Properties
Diphenyl	High[4]	None[4]	Slight[10]	Intense[10]	Moderate[10]	Can be poor[4]
Mono- and di-chlorobenzenes	High[7,8]	None[7]	Toxic[14]	Moderate	Easy[7]	Usually good in enclosed machines[8,15,16]
Methyl salicylate	High[9]	None[9]	Slight[9]	Intense[9]	Difficult	Usually good[9]
o-Phenylphenol	Medium[4]	Slight[4]	Slight[4]	Moderate[4]	Moderate[8,10]	Usually good[4,15]
p-Phenylphenol	Medium	Appreciable[13]	Slight	Slight	Difficult[8]	Good[8]
Phenylmethylcarbinol (+ acetophenone)	Low–medium[8]	None	Slight	Intense	Easy[8]	Usually good; may harshen the fibre[17]
Tetrahydronaphthalene (+ cyclohexanol)	High[7]	Appreciable[7]	Toxic[7]	Moderate[7]	Moderate	Can be poor[7]
Benzoic acid	Low[7]	None[7]	Slight[7]	None[7]	Easy[7] Difficult[8]	May cause specks[7]
Salicylic acid	Low[7]	None[7]	Slight[7]	None[7]	Easy[7]	May cause specks[7]

work by Peters and Sumner leads to the following conclusions—

(i) Water-soluble agents are first adsorbed by the fibre, which is thereby swollen or plasticised, so that dyeing can take place more quickly. These agents compete with dye for available sites in the fibre, and the equilibrium exhaustion of dye is reduced. This phenomenon was observed for benzoic acid by Remington and Schuler[19].

(ii) Water-insoluble agents, in addition to plasticising the fibre, also serve to surround it with a solvent layer in which dye is highly soluble. Dyeing is further accelerated owing to the increased concentration gradient.

Vickerstaff concludes that carriers merely serve the same purpose as raising the temperature, in that the molecular structure is loosened and the rate of dyeing increased.

One possible way in which carriers might act, not considered by Vickerstaff, merits some attention. Although any complex of carrier and dye must have a molecular volume greater than that of the dye, it is conceivable that the rate of diffusion of the dye is controlled, not merely by its molecular volume, but by the various forces between its reactive groups and the fibre; a complex in which these groups were internally neutralised might be expected to diffuse more rapidly into the fibre in spite of the increase in molecular volume. Such a mechanism would obviously be more likely with a carrier containing carboxyl, amino, or hydroxyl groups than with a hydrocarbon.

In practice, the choice of the best carrier from those available is controlled mainly by volatility, ease of application, and effect on light fastness. Volatile carriers like diphenyl and chlorinated benzenes, which do not affect light fastness, can be used successfully on loose staple, slubbing, and yarn in totally enclosed circulating machinery; if used for piece dyeing on the jig or winch, they tend to condense on the cooler parts of the equipment, drop back into the dye liquor, and form spots on the fabric which are impossible to remove. For piece dyeing a carrier of lower

volatility, such as o- or p-phenylphenol, is normally recommended, but such agents affect the light fastness of many valuable disperse dyes on polyester fibres, and a compromise is therefore necessary. Even with o-phenylphenol, which affects the light fastness to a less extent than does the para isomer, spotting troubles are not unknown, and the strictest control of the rate and the temperature at which the free phenol is released is essential to obtain satisfactory results on 100% Terylene. The problem of producing speck-free dyeings with o-phenylphenol on Terylene–wool blended fabrics (§ F) is even more acute, and it has been necessary to use p-phenylphenol in spite of its known defect of reducing the light fastness of certain dyes.

In Table VII three related carriers are compared in practical behaviour, and it will be seen that many conflicting factors must be considered before making a final choice for a particular purpose. The influence of residual carrier in the fibre on the light fastness of Dispersol and Duranol dyes has recently been published[13].

A recent trend in the U.S.A. is the alleged discovery of carriers which are highly efficient at low temperatures (viz. 60–80°c.). It is too early to say whether the claims are justified on the bulk scale, but laboratory experience usually shows that low-temperature efficiency is manifest only with dyes which have relatively high rates of diffusion. Although it may be possible to achieve deep dyeings at 60°c. in 1 hr., it is rarely worthwhile doing so if the final result has poor wet and sublimation fastness. In addition to the minimum requirements of any carrier, a product suitable for such low-temperature work must be capable of yielding heavy depths from the more slowly diffusing dyes of superior fastness; there is no evidence that this is yet possible economically.

Until the perfect dyeing assistant is devised, carrier dyeing is best regarded as a temporary expedient which will enable Terylene to be dyed, with some degree of success, in equipment originally intended for some other fibre where temperatures

Table VII
Practical Properties of Three Related Carriers

Property	Diphenyl (in Tumescal D)	o-Phenylphenol (in Tumescal OP)	p-Phenylphenol (in Tumescal PH)
Melting point	71°c.	54°c.	165°c.
Method of use	Aqueous emulsion	Na salt converted to phenol during dyeing	Aqueous dispersion, or Na salt converted to phenol during dyeing
Quantity employed ...	6–10% on fibre wt.	2–4 parts per 1000 parts of dye liquor	2–4 parts per 1000 parts of dye liquor
Forms of Terylene on which mainly used	Loose staple, slubbing, yarn, half-hose	Loose staple, slubbing, yarn, half-hose, knitted fabric and woven cloth, Terylene–wool yarn	Terylene–wool cloth, subject to light fastness limitations
Suitable equipment ...	Open back, circulating machinery, paddle machinery	Open back, circulating machinery, paddle machinery, jig*, winch, star-frame	All types
Special precautions ...	Keep dyeing temp. > 80°c., otherwise carrier may solidify. Add portionwise	Liberate phenol slowly at 100°c.	None
Method of removal ...	Dry heat, storage	NaOH and Lissapol C at 70–100°c. will remove carrier from fibre surface	As o-phenylphenol
Chief drawbacks ...	Unlevel dyeing; smell	Slight effect on light fastness; complex dyeing process	Appreciable effect on light fastness

* Except for Terylene–wool cloth

above 100°c. are not required. When newer fibres like Terylene become firmly established, the dyer will certainly prefer to instal the most suitable equipment available at the time. In the foreseeable future this is most likely to be high-temperature machinery, operating up to at least 130°c. Interest in carrier dyeing may then be expected to decline.

D— Azoic Dyes

There are four main processes in the application of azoic dyes to textile fibres— (i) application of coupling component, (ii) application of diazo component, (iii) development, and (iv) soaping.

If specific cases of applying azoic dyes are considered, it is found that processes (i) and (ii) or processes (ii) and (iii) may be carried out in one operation. For example, in the most important application of azoic dyes, to cellulosic fibres, processes (ii) and (iii) are simultaneous, whereas with acetate rayon and nylon processes (i) and (ii) are generally simultaneous. Waters first described a method of applying azoic dyes to Terylene[1]. It involved the simultaneous application of the dispersed free base and the dispersed coupling component. Subsequent development was achieved by immersion in a hot solution of nitrous acid. No carrier was used in the application of the azoic components, and the coupling component preferred by Waters was 2:3-hydroxynaphthoic acid. Arylamides of 2:3-hydroxynaphthoic acid (e.g. Brenthols (ICI)) were not found to be of value, as, under the conditions used by Waters, they were not absorbed by the fibre. α- and β-Naphthol could be used, but the colours obtained were very dull and generally the light fastness of the resultant dyeings was poor. Until comparatively recently the method used by Waters was that generally adopted, with only minor modifications, for dyeing Terylene to such important colours as black, maroon, and scarlet.

There is a great deal of quantitative information available on the absorption of azoic components by cellulosic fibres[20] and some for nylon and acetate rayon[21,22]. As yet, however, little quantitative information has been published on the absorption of azoic components by Terylene fibre. The production of complete data will take many years, but a start has been made, and some of the information obtained is presented in this paper.

1. Absorption of 2:3-Hydroxynaphthoic Acid

In spite of recent developments in the use of other coupling components, 2:3-hydroxynaphthoic acid is still the only general coupling component employed where high-temperature dyeing machinery is not available, or when scarlets and reds are being dyed. Factors which may well affect the quantity of 2:3-hydroxynaphthoic acid absorbed into the Terylene are— temperature of application, time of application, liquor : goods ratio, quantity of 2:3-hydroxynaphthoic acid in the application bath, and pH of application bath. These variables have been investigated and the results are shown in Fig. 1. The amount of 2:3-hydroxynaphthoic acid absorbed was determined by measuring the optical density, in the ultraviolet (350 mμ.), of an o-chlorophenol solution of bright Terylene containing the coupling component. At this selected wavelength 2:3-hydroxynaphthoic acid strongly absorbs ultraviolet radiation and Terylene dissolved in o-chlorophenol is still completely non-absorbing. The quantity of 2:3-hydroxynaphthoic acid absorbed could be found by comparing the optical density with the value obtained for a standard solution containing the same amount of bright Terylene but no coupling component.
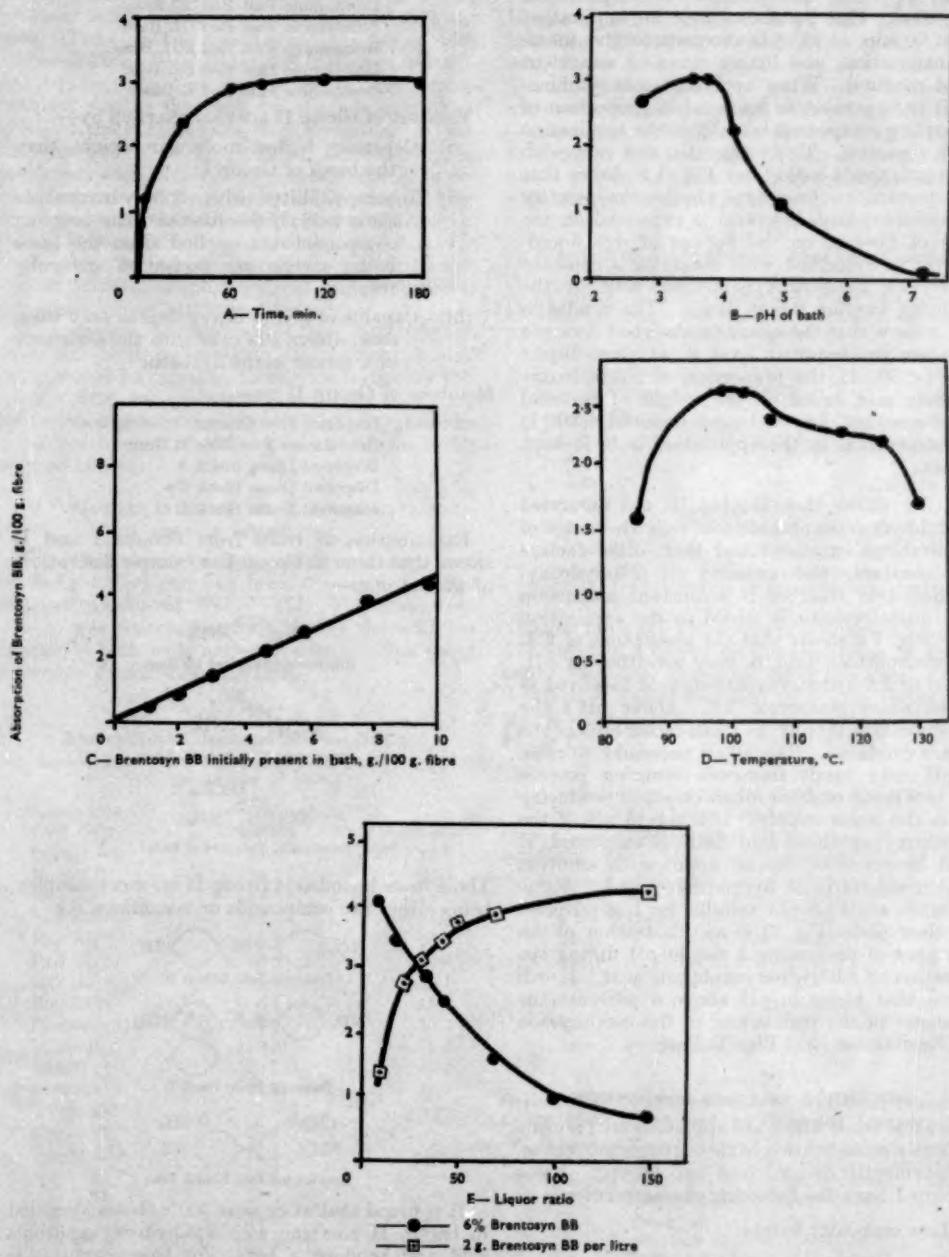
Standard conditions— 6% Brentosyn BB from 30 : 1 liquor for 90 min. at 95°C. and pH 3-8

FIG. 1— Factors influencing the Absorption of Brentosyn BB into Terylene

Fig. 1 D shows that, with a time of application of 90 min., a temperature of 98°C. gives maximum exhaustion, and there is, therefore, nothing to gain by applying this product at temperatures above 100°C. Fig. 1 A shows that an application time of 60 min. at 98°C. is adequate to give maximum exhaustion, and longer times of treatment are not required. When applying azoic combinations it is important to know what proportion of the coupling component initially in the application bath is absorbed. This proportion can vary with the liquor : goods ratio, and Fig. 1 E shows that the proportion is not constant whether the quantity of 2:3-hydroxynaphthoic acid is expressed on the weight of fibre or on the volume of dye liquor. The dyer is concerned with obtaining a constant quantity of 2:3-hydroxynaphthoic acid in the fibre using varying liquor ratios. The results in Fig. 1 E show that the quantity absorbed does not fall below the required level if, at short liquor ratios (< 30 : 1), the proportion of 2:3-hydroxynaphthoic acid based on the weight of material is kept constant, but at longer liquors (> 30 : 1) its concentration in the application bath is kept constant.

Fig. 1 C shows that Terylene is not saturated with 2:3-hydroxynaphthoic acid over the range of concentrations examined and that, other factors being constant, the quantity of 2:3-hydroxynaphthoic acid absorbed is a constant proportion of the quantity initially added to the application bath. Fig. 1 B shows that the absorption of 2:3-hydroxynaphthoic acid is very sensitive to pH. The pH of 2:3-hydroxynaphthoic acid dissolved in distilled water is approx. 3·8. Above pH 4 the exhaustion falls rapidly, as alkali-metal salts of the acid are produced. The alkali necessary to raise the pH may result from the scouring process prior to dyeing or from alkali or alkali-producing salts in the water supply. If a rise in pH of the 2:3-hydroxynaphthoic acid bath is suspected, it should be corrected by an appropriate addition of either sulphuric or hydrochloric acid. Acetic and formic acids are not suitable for this purpose. The colour-plate (Fig. 2) is an illustration of the importance of preventing a rise in pH during the application of 2:3-hydroxynaphthoic acid. It will be seen that a rise in pH above 4 prevents the attainment of the true colour of the combination with Brentamine Fast Blue B Base.

2. ABSORPTION OF DIAZO COMPONENTS

The azoic bases which are applicable to Terylene can, from a consideration of their dyeing properties, be conveniently divided into two groups. Bases of Group I have the following characteristics—

(i) Low molecular weight

(ii) Compatibility with 2:3-hydroxynaphthoic acid, so that the base and the coupling component may be applied from the same bath

(iii) Rapid diffusion into the fibre, so that the use of dyeing temperatures above 100°C.

or the addition of a carrier to the dye-bath is not required.

The following bases are included in Group I—

     Brentamine Fast Red 2G Base
     Brentamine Fast Red GL Base
     Brentamine Fast Red 3GL Base
     Brentamine Fast Red RL Base
     Brentamine Fast Red B Base.
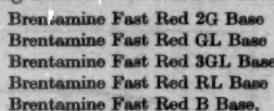
Members of Group II are characterised by—

(i) Generally higher molecular weight than the bases of Group I

(ii) Incompatibility with 2:3-hydroxynaphthoic acid; if the base and the coupling component are applied from the same bath, severe tar formation generally results.

(iii) Capable of giving heavy depths only when dyed above 100°C. or with the assistance of a carrier in the dyebath.

Members of Group II are—

     Dispersol Fast Orange G (borderline)
     Brentamine Fast Blue B Base
     Dispersol Diazo Black A
     Dispersol Diazo Black 2B
     Dispersol Diazo Black B
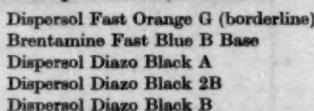
Examination of bases from Groups I and II shows that those in Group I are simple derivatives of aniline, e.g.—

Brentamine Fast Red 2G Base

Brentamine Fast Red GL Base

Brentamine Fast Red B Base
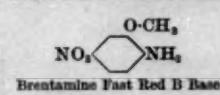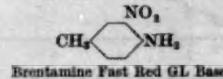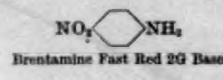
Those bases included in Group II are more complex, being either azo compounds or benzidines, e.g.—

Dispersol Fast Orange G

Dispersol Diazo Black B

Brentamine Fast Blue B Base
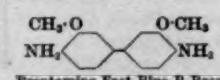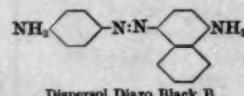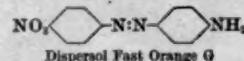
It is found that at or near 100°C. bases classified in Group II combine with 2:3-hydroxynaphthoic acid and produce a tar. For this reason it is standard practice to apply the base first and then, after an intermediate rinse, apply the 2:3-hydroxynaphthoic acid from a separate bath. With this method tar formation is reduced to a minimum, and the tar which is produced results from the slight bleeding out of the base from the Terylene

during the application of the coupling component. No detailed work on the chemistry of the formation of this tar has been carried out, but it is suspected to be connected with the formation of a salt between the 2:3-hydroxynaphthoic acid and the base. Thus, in the production of a black with Dispersol Diazo Black B and 2:3-hydroxynaphthoic acid, preventing the formation of the violet-coloured salt of the base, by the addition of an alkali, largely eliminates the formation of tar. This method is of no practical interest, for, as previously seen, 2:3-hydroxynaphthoic acid is not absorbed into Terylene under alkaline conditions. It is probable that the much lower strength of Group I bases, resulting from the presence of a nitro group for example, prohibits salt formation with 2:3-hydroxynaphthoic acid and so removes the possibility of tar formation.

A reduction in acidity of the 2:3-hydroxynaphthoic acid by blocking the carboxylic acid group would be expected to provide a cure for this trouble with bases classified in Group II. This behaviour has been confirmed with the arylamides of 2:3-hydroxynaphthoic acid, which are compatible with all bases.

3. FACTORS INFLUENCING THE ABSORPTION OF DIAZO COMPONENTS

The exhaustion of a range of Brentamine Fast Bases into Terylene has been determined under standard conditions (Table VIII). The exhaustion of base was determined by titrating the acidified exhausted bath with sodium nitrite solution using potassium bromide as a catalyst.

TABLE VIII
Absorption of Brentamine Fast Bases

(6% Base + Lissapol C Paste (1 g./litre) at 30 : 1 liquor ratio for 90 min. at 98°c.)

Brentamine Fast Base	Exhaustion (%) No Carrier	8% Tumescal D
Orange GR	25·8	25·1
Scarlet G	29·5	27·0
Red 2G	18·0	8·0
Red 3GL	53·3	54·5
Red RL	28·9	26·3
Red GL	43·5	40·4
Red B	30·8	39·1
Red LTR	6·1	18·5
Bordeaux GP	31·5	30·7
Violet B	10·0	16·5
Blue B	20·2	44·3
Blue 2B	27·4	44·0
Yellow GC*	22·5	—
Orange GC*	25·1	—
Scarlet 2G*	13·2	—
Scarlet RC*	17·2	—
Red KB*	36·8	—
Red FR*	74·2	—
Red RC*	37·1	—
Garnet GBC*	53·5	—

* Commercially available as water-soluble salts. Dyebaths neutralised with dilute sodium hydroxide solution before application.

The results in Table VIII show that the exhaustion of simple Group I bases into Terylene is generally low, and in only three cases is an exhaustion greater than 50% obtained. It will be seen that

the addition of Tumescal D (a preparation of diphenyl) to the bath does not produce a significant change in the exhaustion of the bases with the exception of Brentamine Fast Red LTR Base, Brentamine Fast Blue B Base, and Brentamine Fast Blue 2B Base. It is therefore thought that, with those bases which show a low exhaustion (generally bases in Group I), the cause is their low affinity for Terylene and not a low rate of diffusion. Confirmation is obtained by the results in Table IX, from which it is seen that dyeing at temperatures above 100°c. does not result in an improved yield with this particular type of base.

TABLE IX
Strength of Azoic Dyeings after Development

(6% Base + 6% 2:3-hydroxynaphthoic acid applied from 30 : 1 liquor containing Lissapol C Paste (1 g./litre) for 90 min. by single-bath method. Normal method of development)

Brentamine Fast Base	Ratio of Depths* 120°c. / 98°c.	130°c. / 98°c.
Orange GR	0·67	0·61
Scarlet G	0·76	0·53
Red 2G	0·67	0·48
Red 3GL	0·83	0·39
Red RL	0·92	0·59
Red B	0·86	0·66
Red LTR	0·80	0·69

* Measured by dissolving known quantities of dyed Terylene in o-chlorophenol and determining the optical density at wavelength of maximum absorption.

Bases in Group II behave in a different manner. The effect of a carrier on the absorption of Brentamine Fast Blue B and 2B Bases has already been detailed. Tables X and XI give additional information on the behaviour of Dispersol Diazo Black B.

TABLE X
Absorption of Dispersol Diazo Black B into Terylene

(6% Dispersol Diazo Black B 300 from 30 : 1 liquor containing Lissapol C Paste (1 g./litre) for 90 min.)

Temp. (°c.)	Carrier	Absorption (g./100 g. fibre)	Exhaustion (%)
76	—	0·42	7
85	—	1·4	24
98	—	4·0	67
113	—	5·1	85
135	—	4·5	75
98	8% Tumescal D	5·2	87

TABLE XI
Strength of Developed Azoic Blacks from Dispersol Diazo Black B applied at Different Temperatures

(6% Dispersol Diazo Black B 300 for 90 min. and 6% 2:3-hydroxynaphthoic acid for 60 min. (applied at 98°c.); liquor ratio 30 : 1; two-bath process; Lissapol C Paste (1 g./litre) in each bath)

Temp. of Application of Base (°c.)	Relative Intensity of Black*
98	0·61
110	1·0 (control)
120	0·98
130	0·87

* Measured by dissolving known quantities of dyed Terylene in o-chlorophenol and determining the optical density at the wavelength of maximum absorption.

The results in Tables X and XI do not completely agree with the behaviour observed in practice, and the cause of this discrepancy has not been determined. The results do show, however, the gross effects obtained by dyeing with a carrier or at temperatures above 100°c.

4. ABSORPTION OF ARYLAMIDES OF 2:3-HYDROXYNAPHTHOIC ACID

The cause of tarring in the application of azoic dyes to Terylene has already been discussed. The conclusion was reached that it might be possible to apply Group II bases by a one-bath process using coupling components with no free carboxyl group, viz. Brenthols. Waters [1] found that, under the conditions he used, Brenthols were not absorbed into Terylene. At that time, however, high-temperature dyeing machinery was not generally available, and the problem has now been re-examined to include application temperatures up to 130°c.

Before the absorption of Brenthols into Terylene was measured, the compounds were checked for stability at 130°c. This was determined by comparing the ultraviolet absorption curves of the sodium salts of the Brenthols dissolved in methyl alcohol before and after heating their aqueous dispersions at 130°c. for 30 min. All the Brenthols in Table XII showed less than 10% decomposition under these conditions, with the exception of Brenthol AT, which is not an arylamide but an acetoacetic ester.

Table XII gives a list of Brenthols and their exhaustion into Terylene when applied at 98°c., with and without a carrier, and at 130°c.

TABLE XII
Absorption of Brenthols into Terylene

(6% Brenthol from 30 : 1 liquor containing Lissapol C Paste (1 g./litre) for 90 min.)

Brenthol	Wavelength of Measurement (mμ.)	Exhaustion (%)* No Carrier At 98°c.	8% Tumescal D	At 130°c.
AN	400	21	26	52
AS	400	4	5	19
AT	—	42	8	**
BA	320	3	2	18
BB	311	1	22	22
BC	398	3	8	36
BN	320	4	14	37
BT	360	15	27	61
CT	310	8	2	20
DA	342	1	1	3·7
FO	320	4	12	48
FR	315	7	44	81
GB	300	2	13	33
MA	310	2	6	33
MN	311	4	4	34
NG	266	2	12	9·8
OT	310	2	9	41
PA	312	1	5	36

* Measured by determining the optical density in the ultraviolet
** Decomposed

The absorption of a few selected Brenthols into Terylene over a range of temperatures has been determined, and the results (Fig. 3 A–H) show that the exhaustion increases as the temperature of application is raised from 100°c. to 130°c. Therefore, in practical dyeing, a temperature of 130°c. will be highly desirable. The building-up properties of selected Brenthols applied to Terylene have been studied, and Fig. 4 A–I shows that several Brenthols effectively saturate the fibre at a comparatively low concentration.

These results (Fig. 4) also indicate the maximum quantity of Brenthol that can profitably be added to a dyeing system if the heaviest possible depth is desired. It must, however, be remembered that the measurements of build-up were obtained under one particular set of conditions. Liquor ratio and quantity of dispersing agent used will probably influence the relationship between Brenthol added to the dyebath and Brenthol absorbed into the fibre. The effect of variation in liquor ratio on the absorption of Brenthol FO has been studied, and the results (Table XIII) show that with this particular Brenthol a change in liquor ratio does not have a severe effect upon exhaustion.

TABLE XIII
Effect of Liquor Ratio on the Absorption of Brenthol FO

(6% Brenthol FO; Lissapol C (1 g./litre); 90 min. at 130°c.)

Liquor Ratio	Absorption (g./100 g. fibre)	Exhaustion (%)
15 : 1	2·6	43
22·5 : 1	2·6	43
45 : 1	2·8	47
90 : 1	2·7	45
180 : 1	2·3	38

If the concentration of Lissapol C is increased, as is sometimes desirable when package-dyeing with Brenthols, the increased solubility of the Brenthol may result in reduced exhaustion, particularly of long liquors. As yet, the effect of a change in liquor ratio has been examined only with Brenthol FO. The behaviour of other Brenthols may be radically different.

The rates of absorption of Brenthol AS and Brenthol BT into Terylene have been studied, and the results are given in Fig. 5. It has not been decided whether the low exhaustion with Brenthol AS is caused by a low saturation value of the Brenthol in the fibre or by a low rate of diffusion into the fibre.

5. UTILISATION OF BRENTHOLS IN PRACTICAL DYEING

A comprehensive evaluation of all possible combinations of azoic bases and those Brenthols which are highly substantive to Terylene has not yet been completed. Preliminary work has shown that possible interesting combinations are—

Brentamine Fast Blue B
Base→Brenthol FO (navy blue)
Dispersol Diazo Black 2B→Brenthol BT (dark brown)
Dispersol Diazo Black B→Brenthol OT (black)
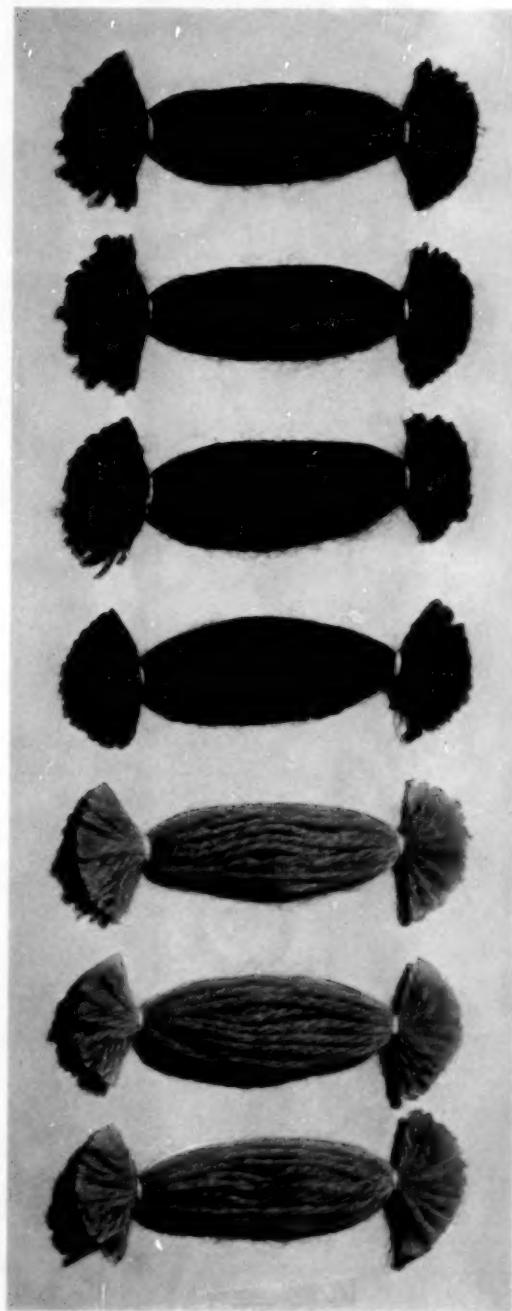
Fig. 2— Effect of pH of Coupling Component Bath on Colour of Brentamine Fast Blue
B Base→2:3-Hydroxynaphthoic Acid applied to Terylene by a Two-bath Process (Base
applied from First Bath at pH 7·1–7·3) and developed at 85°C. with Acidified Sodium Nitrite
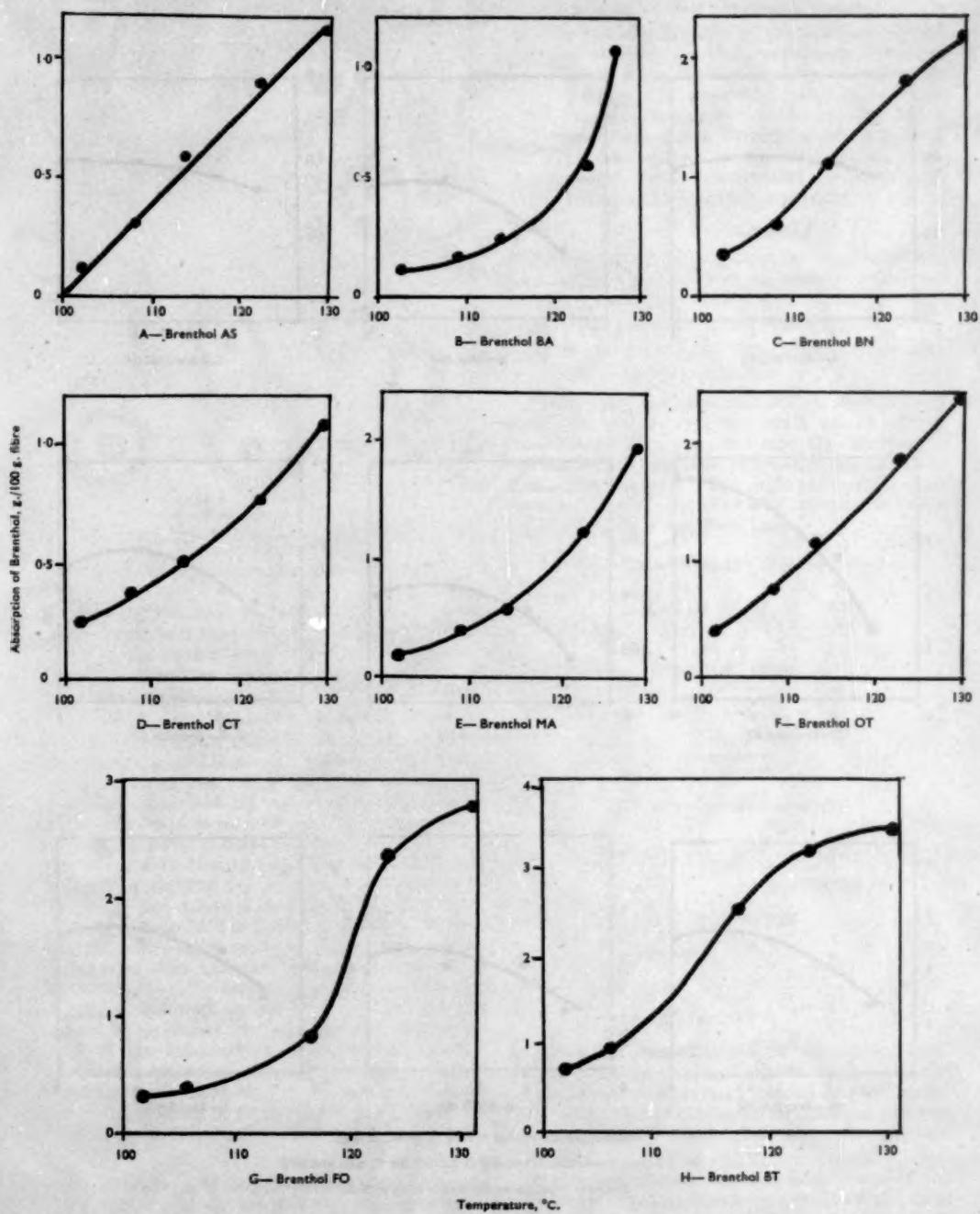
6% Brenthol from 30 : 1 liquor containing Lissapol C (1 g./litre) for 90 min.

FIG. 3— Effect of Temperature on the Absorption of Brenthols into Terylene
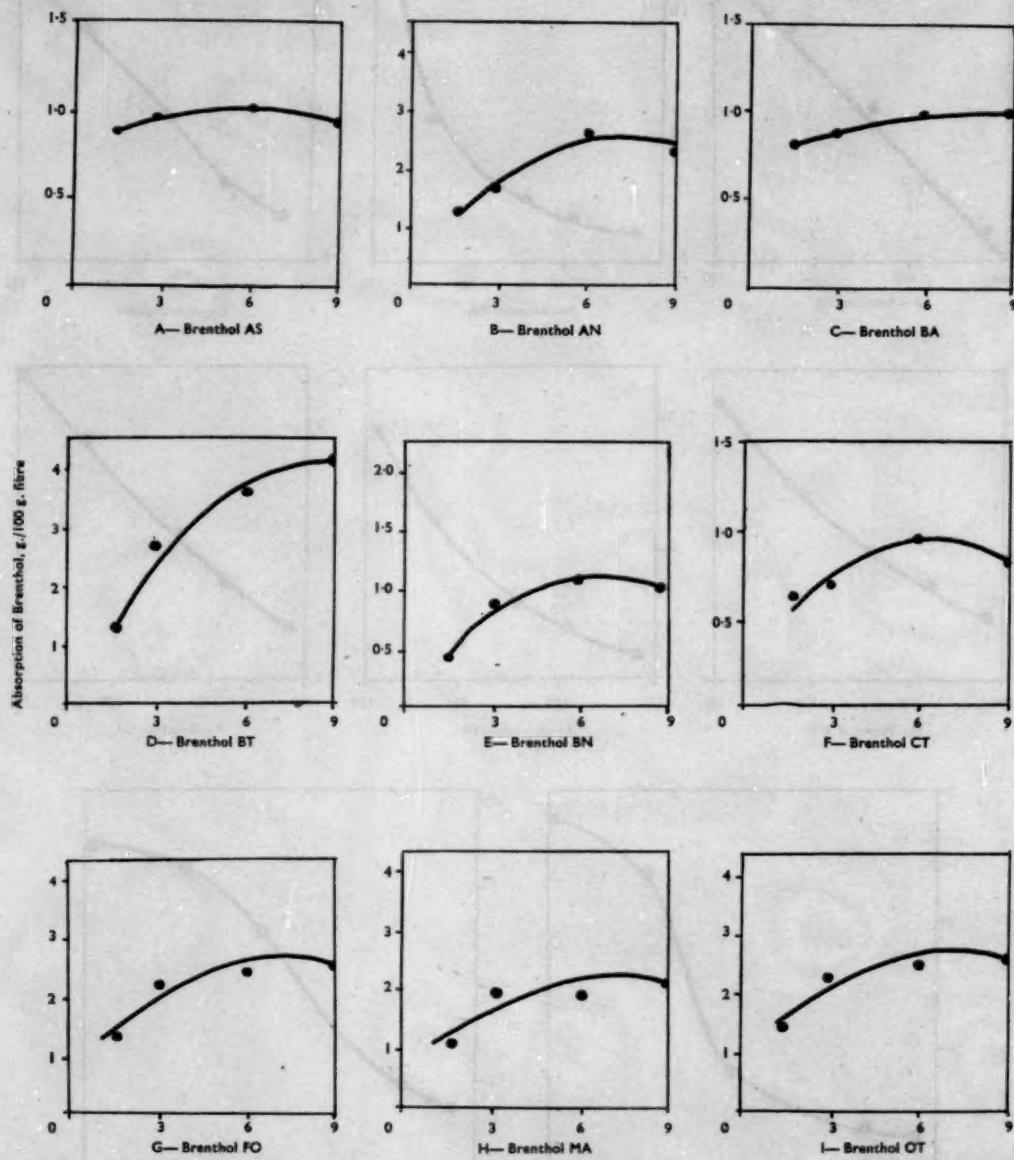
Brenthol initially present in bath, % on wt. of fibre

30 : 1 Liquor containing Lissapol C (1 g./litre) for 90 min. at 130°C.

FIG. 4— Building-up Properties of Brenthols
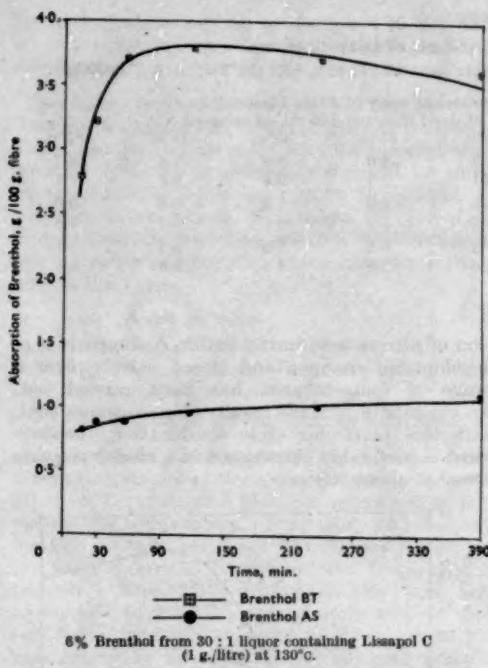
Fig. 5— Rate of Absorption of Brenthols into Terylene

6% Brenthol from 30 : 1 liquor containing Lissapol C
(1 g./litre) at 130°c.

———⊞——— Brenthol BT
———●——— Brenthol AS

A full study has been completed only in the case of the black, and since the process was first introduced to the dyeing trade [23], many thousands of pounds of Terylene has been satisfactorily dyed with this combination.

In outline, the process consists in applying 12% Dispersol Diazo Black BS Paste in a dyebath containing 2 g. of Lissapol C Paste per litre of dye liquor for 15 min. at 120°c. Brenthol OT (2·5%), previously dispersed in water containing 0·10% Lissapol C Paste, is then added. The temperature is raised to 130°c., and dyeing continued for 60 min. The dyebath is dropped, and the material rinsed in liquor containing 1 g. of caustic soda (68°Tw.) per litre. The colour is then developed in a fresh bath containing 14% of hydrochloric acid (32°Tw.) and 8% of sodium nitrite. The treatment is commenced cold and the temperature raised to 85–95°c. as rapidly as possible. At least 30 min. should be allowed at 85–95°c. Normally the process is concluded by "soaping" for 10 min. at 60–80°c. In cases where clean dyeings are not produced, a reduction–clearing treatment (in 2 g. of sodium hydrosulphite, 2 g. of caustic soda, and 2 g. of Lissolamine A (50%) per litre of liquor for 20 min. at 60–70°c.) prior to "soaping" is of very great value.

The advantages of the process based on Dispersol Diazo Black B and Brenthol OT compared with the black obtained from Dispersol Diazo Black B and 2:3-hydroxynaphthoic acid are—

(a) Dyeing costs are reduced because less dye, coupling components, and auxiliary products are required

(b) Dyeing costs are reduced because the total dyeing time is reduced by one-third to one-half of that previously required

(c) The rubbing fastness of the resultant dyeing is superior to that previously obtained. In addition to the obvious advantage in fastness for domestic purposes, the increased cleanliness of the dyeing is of importance when Terylene slubbing is dyed, as loose colour on the fibre surface often results in a deterioration in subsequent gilling and recombing properties.

6. DEVELOPMENT

The process of development for azoic combinations applied to Terylene is usually considered to take place in two stages—

(i) "Diazotisation" of the base

(ii) Coupling of the "diazotised" base with the coupling component.

A study has not been made of the chemistry of these two stages, and the exact nature of the "diazotised" base absorbed into the Terylene is not known. There is an alternative possibility to that outlined above. The azoic pigment could be produced by reaction of the nitroso coupling component with the free base—

A— "NORMAL" METHOD
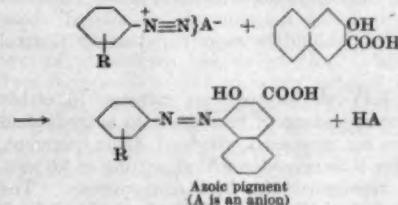
B— ALTERNATIVE POSSIBILITY
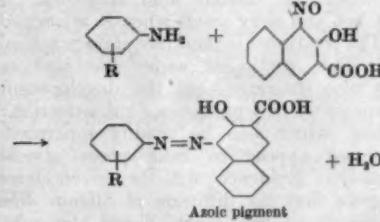
In the second possibility the nitroso coupling component could be produced within the fibre by the action of hot nitrous acid instead of the "diazotised" base. The evidence so far obtained suggests that reaction B does not take place within Terylene.

A detailed examination has been made of the conditions affecting the development of the azoic pigment—

Brentamine Fast Blue B Base→Brenthol FO

Bright Terylene yarn was treated for 90 min. with 4% of the Base and 4% of the Brenthol in a bath containing 2 g. of Lissapol C Paste per litre. The

TABLE XIV

Effect of Time, Temperature, and pH of Diazotisation

Brentamine Fast Blue B→Brenthol FO (Open vessel; liquor ratio 30 : 1; 12% HCl (32°Tw.) + 8% NaNO₃)

Time in HNO₃ (min.)	NaAc*	Optical Density of Azoic Pigment (per gram of dyed fibre per 100 ml. of solvent)						
		25°c.	35°c.	45°c.	55°c.	65°c.	75°c.	85°c.
20	No	1·1	1·7	2·7	5·0	5·9	7·6	8·7
	Yes	1·8	3·1	4·1	5·8	6·8	8·1	9·1
40	No	1·6	3·0	4·6	6·0	7·5	8·6	9·0
	Yes	3·1	4·6	6·2	7·4	8·1	9·7	9·5
60	No	2·0	3·3	5·2	6·5	7·8	8·7	9·3
	Yes	3·7	5·1	6·5	7·8	8·4	9·5	9·8

* Aftertreated in 2 g. sodium acetate for 90 min. at 95°C.

material containing the absorbed azoic components was practically colourless, whilst the developed dyeing was a dull blue with a maximum absorption of visible light, when it was dissolved in o-chlorophenol in presence of dissolved Terylene, at a wavelength of 585 mµ. The development of the azoic pigment was studied quantitatively by measuring the optical density at 585 mµ. of solutions of a known concentration of Terylene which contained the absorbed azoic components subsequently given the developing treatment.

The effects of time and temperature of treatment in acidified sodium nitrite were studied, and the results are given in Table XIV, which also shows the effect of aftertreating the developed yarn in a solution of sodium acetate, since it was reasoned that the coupling reaction of "diazotised" base and Brenthol should be more rapid under neutral conditions.

Table XIV shows that an increase in either time or temperature of treatment in nitrous acid results in an increased yield of azoic pigment. In practice it is considered that a time of 40 min. at 85°c. represents the best compromise. The results also show that the effect of adding sodium acetate after the treatment in nitrous acid is negligible when the nitrous acid treatment is carried out hot and very small when it is carried out cold. The treatment is therefore of no practical value with this particular azoic combination. This result also indicates that the development does not consist of two processes, "diazotisation" and coupling, which can be readily separated. Both processes appear to take place almost simultaneously. Evidence will be given later which suggests that the diffusion of nitrous acid into the fibre is an important, if not the only, process controlling the rate of development.

During development in an open vessel there is a copious evolution of nitrous fumes which can prove very troublesome. In addition to the obvious drawback of a possible health hazard, it is also undesirable as it results in the removal of much of the nitrous acid from the bath before development is complete within the Terylene. If development is carried out in a closed pressure vessel, however, no loss of nitrous fumes from the system is possible, and improved yields of azoic pigment are obtained by allowing the temperature to be raised whilst maintaining the required concentra-

tion of nitrous acid in the bath. A comparison of development in open and closed vessels, over a range of temperatures, has been carried out. An examination of the results (Fig. 6) shows that, with this particular azoic combination, development is preferably carried out in a closed pressure vessel at about 100°c.

Development with 12% hydrochloric acid (32°Tw.) + 9% sodium nitrite for 40 min.
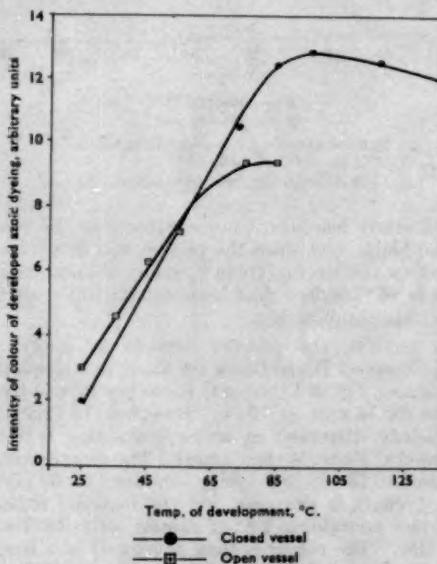
Fig. 6— Effect of Temperature upon Development of 4% Brentamine Fast Blue B Base plus 4% Brenthol FO applied to Terylene

A similar series of tests has been carried out with the combination—

Dispersol Diazo Black B→Brenthol OT

and the conclusions reached are identical with those obtained with Brentamine Fast Blue B Base and Brenthol FO.

7. FASTNESS OF AZOIC COMBINATIONS

It is not possible to generalise, at this stage, on the light fastness of azoic combinations. Certain combinations, when applied to Terylene, give low light fastness, whilst other combinations result in very high fastness to light. Unlike the behaviour on cellulosic fibres and acetate rayon, the light

fastness of azoic combinations applied to Terylene is not affected by "soaping" subsequent to development.

For many purposes, it is important that the dyed Terylene should be fast to severe pleating processes. For example, the Terylene may be blended with wool, and the fabric ultimately steamed for times up to 30 min. and pressures up to 10 lb./sq.in. to set the pleats. Lack of fastness of azoic-dyed Terylene can be caused by one or a combination of the following compounds, which may be present within the fibre—

(a) Azoic pigment

(b) Free coupling component

(c) Nitrosated coupling component

(d) Free base

(e) "Diazotised" and decomposed base

It has been demonstrated that, under very severe steaming conditions, azoic combinations will blind on Terylene as a result of migration of pigment to the fibre surface. The conditions necessary for this to take place are usually too severe for the phenomenon to be encountered frequently in practice. Free 2:3-hydroxynaphthoic acid and arylamides of 2:3-hydroxynaphthoic acid are not sufficiently intensely coloured to give a poor fastness rating by heavily staining adjacent undyed fibres. Although nitrosated 2:3-hydroxynaphthoic acid and arylamides of 2:3-hydroxynaphthoic acid are generally more intensely coloured than the un-nitrosated compounds, they are less intensely coloured than the azoic pigments; moreover, tests have shown that these compounds are extremely fast and are not readily removed from Terylene by steaming. Free bases, however, diffuse out readily from Terylene and stain adjacent white fibres heavily. For this reason their presence can result in the final dyeing showing inadequate fastness properties. Fortunately, after reacting with nitrous acid the free bases possess significantly better fastness to dry heat or steaming (Table XV).

Where maximum fastness (freedom from staining adjacent undyed fibres) is required, the following precautions should therefore be taken—

(i) The excess of base over coupling component should be either completely eliminated or at least reduced to a minimum

(ii) The reaction with nitrous acid should be as complete as possible

(iii) In certain cases the bases used, e.g. Brentamine Fast Blue B Base, are practically colourless, and this type of product obviously allows dyeings to be produced which are extremely fast to steaming and dry heat treatments.

TABLE XV
Effect of the Development Process on the Sublimation Fastness of Free Bases applied to Terylene

Base	Material*	Sublimation (staining of adjacent Terylene)	
		15 sec. at	
		170°c.	220°c.
Brentamine Fast Red B Base	U	3	2
	D	5	3
Brentamine Fast Red 3GL Base	U	3	1
	D	5	3
Brentamine Fast Red 2G Base	U	4	3
	D	5	3
Dispersol Diazo Black B	U	4	3
	D	5	3

* U = Untreated
  D = Treated with HCl + NaNO₂ as used for development

In general the work carried out on the application of azoic dyes has shown that this range of dyes represents a very valuable method of dyeing Terylene, but much information is still required before the range of colours is increased and before greater reproducibility in colour and fastness properties is realised.

E— The Dyeing of Polyester Fibre-Wool Blends

Some problems in the dyeing of mixtures of Terylene and wool have recently been discussed by Fern and Hadfield [24], and this subject has also received much attention in the U.S.A.[7, 8, 25–28]. The main difficulties associated with yarn- or piece-dyeing such blends arise because all disperse dyes for the polyester component stain wool; this

TABLE XVI
Fastness of Dyed Wool* and Terylene-Wool† (Heavy Depths)

		Washing (once at 55°c.)			Perspiration			Water		
		Effect on Pattern	Staining of Terylene	Staining of Wool	Effect on Pattern	Staining of Terylene	Staining of Wool	Effect on Pattern	Staining of Terylene	Staining of Wool
Red	Wool	4–5	5	5	5	5	4	5	5	3–4
	Terylene–wool	4	2–3	2–3	4–5	2	2	4–5	2–3	2–3
Brown	Wool	4–5	5	5	5	5	4–5	5	5	3–4
	Terylene–wool	4–5	2	1	4–5	3	1	4–5	3	1
Navy	Wool	4–5	5	5	5	5	5	5	5	4
	Terylene–wool	4–5	1	1	4–5	2	1	4–5	2	1
Black	Wool	4–5	5	5	5	5	4–5	5	5	4
	Terylene–wool	4–5	2	2	5	2	2	5	2	2

* The wool was piece-dyed (to match the Terylene–wool) with chrome dyes under laboratory conditions (afterchrome process)

† The Terylene–wool was piece-dyed under semi-bulk conditions with disperse and acid milling dyes, with permanganate and scouring after-treatments.

makes shade-matching troublesome, necessitates an additional clearing process for heavy depths, and gives dyeings which are generally poor in fastness to wet treatments and rubbing. The degree of staining is not significantly affected by simple variations in dyebath acidity or by the presence of auxiliary products [24, 29]. The stain cannot be completely removed without seriously degrading the wool, and, in heavy dyeings particularly, the wet fastness properties of piece-dyed Terylene–wool are much inferior to what would be expected if the material were produced from the components dyed separately as loose staple or slubbing and subsequently blended. Some typical fastness results are shown in Table XVI, from which it is seen that the wet fastness of Terylene–wool is much lower, especially in terms of the staining of adjacent material, than that of chrome dyes on wool, which is considered by many to typify the desired degree of fastness for this class of material.

The initial work on Terylene–wool was done with acid levelling or acid milling dyes for the wool [4], since the blend could then be dyed by a single-bath method. By dyeing with the aid of a carrier at 100°c., the staining of wool was minimised. o-Phenylphenol was originally chosen as the best carrier, since it did not greatly affect the light fastness of many disperse dyes on Terylene, and because it was thought suitable for large-scale application to these fabrics in the winch.

It is now known [24] that o-phenylphenol is extremely difficult to use in bulk on Terylene–wool piece-goods, although satisfactory results are being obtained on blended yarns in circulating machinery. In the winch, the o-phenylphenol must be added as the sodium salt and neutralised with acetic acid, in presence of Lissapol C, at a low temperature (not above 40°c.) before the fabric is entered; if it were neutralised at 100°c. during dyeing, as for 100% Terylene, the wool would dissolve. Even when the free phenol is liberated as a fine dispersion and the temperature is carefully raised to 100°c. after the material has been entered, there is a tendency for unabsorbed carrier to aggregate during the change of phase which occurs at the melting point, 54°c. This may lead to tarry specks of carrier and heavily dyed spots on the cloth. An alternative method of neutralising sodium o-phenylphenoxide involving diammonium phosphate [39] appears to eliminate the possibility of the o-phenylphenol becoming aggregated.

p-Phenylphenol, with a much higher melting point than the ortho isomer, can be used successfully under bulk conditions to give dyeings free from carrier or dye spots. It is added as an aqueous dispersion, and the only drawback to its use is the present lack of a complete range of suitable disperse dyes with which it can be used. The light fastness of Duranol Red X3B, a useful red component for Terylene–wool, is reduced by p-phenylphenol, but Duranol Red 2B can be used instead, with Dispersol Fast Yellow GR and Duranol Blue G. Duranol Red 2B, however, lowers the sublimation and pleating fastness of the final dyeing,

and cannot be indiscriminately recommended. Details of the process are as follows—

The scoured material is run in the cold dyebath. Lissapol C Paste (2 parts), sodium or potassium dihydrogen phosphate (0·2–0·4 part)*, Tumescal PH (3 parts)†, and Glauber's salt crystals (16 parts per 1000 parts of liquor) are added separately to the dyebath. The temperature is raised to 40°c. in approx. 15 min. The dispersed, sieved disperse dyes and the dissolved, sieved acid dyes are added. The temperature is raised to 100°c. in 45 min. and dyeing is continued for at least 60 min.‡ The bath is cooled, and the material rinsed in cold water and finally scoured in a bath containing 1 part of Lissapol C Paste per 1000 parts of liquor at 50–60°c. for 15 min. A final thorough rinsing in cold water concludes the process. If shading additions are necessary, these are made after dyeing for 45 min. at 100°c., at least 30 min. being allowed after each addition.

A position has therefore been reached where a satisfactory technique has been evolved for piece-dyeing blends of Terylene and wool, but where the inherent staining of wool by existing disperse dyes, and the influence of the most satisfactory carrier on their light fastness, prohibit the widest use of the method. Even if the wool stain is kept to a minimum by dyeing at 100°c. for a sufficient time and aftertreating, the wet fastness of most medium and heavy depths will be too low for most purposes. This difficulty has been stressed by Luttringhaus [26], who states that it takes about 12 hr. to complete a navy or black dyeing on Dacron–wool, much of this time being taken up with scouring operations between the application of disperse dyes to the Dacron and chrome dyes to the wool.

Even if the practical disadvantages of a two-stage dyeing process are accepted, and chrome dyes are used for the wool in these blends, the final wet fastness will probably not be improved to a sufficient extent, and will certainly still be less than that of chrome dyes on 100% wool owing to the disperse dye stain. Furthermore, many disperse dyes on wool (although not inside Terylene) can form differently coloured chrome complexes when subjected to the afterchroming treatment: thus, Duranol Red X3B and Duranol Red 2B go blue-grey, and this makes shade-matching very complex.

It is clear that any major advance in this field must await the discovery of either (a) a range of disperse dyes which possess adequate light and sublimation fastness when dyed with p-phenylphenol, and which do not stain wool, or (b) a restraining agent which can be used with existing disperse dyes to prevent them from staining wool [28]. Until then,

---

* Sodium or potassium dihydrogen phosphate is used to control the dyebath pH in the range 6·5–7·5. It is necessary to neutralise traces of alkali in the fabric, or of alkali or alkali-producing salts in some water supplies.

† Tumescal PH is dispersed by stirring 1 part of the powder in 3–10 parts of cold water containing a little dissolved Lissapol C Paste. The mixture is then heated to 100°c., and added to the dyebath.

‡ The use of fully enclosed stainless-steel dyeing vessels is recommended. If open vessels are used, the lower dyeing temperature which results causes heavier staining of the wool by disperse dyes, and a consequent lowering of the rubbing, pleating, and sublimation fastness of the final dyeing.

piece-goods should be dyed only in pale colours and certain medium depths, and the fastness properties should be thoroughly checked and approved before undertaking bulk production.

Luttringhaus[26] has described a novel two-bath method of dyeing Dacron–wool blends with disperse dyes followed by esters of leuco vat dyes for the wool. The vat esters are applied in presence of formic acid and sodium formaldehyde-sulphoxylate after the Dacron has been dyed, and these agents help to remove the disperse-dye stain from the wool. The results of bulk experiments by this method will be awaited with interest, but it may be predicted from the behaviour of esters of leuco vat dyes on 100% wool that the main difficulties will be—

(i) High cost of all except pale colours

(ii) Difficulty of achieving good rubbing fastness

(iii) Difficulty of development

(iv) Effect of the stripping process on the colour of the dyed Terylene, which may make shade-matching difficult.

In another method of dyeing Dacron–wool, padding of vat pigments on the fabric with the aid of a latex is followed by reduction, re-oxidation, and cross-dyeing of the wool component [27]. No indication of fastness properties is given.

The dyeing of Dacron–wool blends at temperatures above 100°c. has also been examined [7], and fabric has been successfully dyed with disperse and Chromacyl (DuP) dyes on the Barotor (DuP) machine at 120°c., with an addition of formaldehyde to protect the wool against attack, and at pH 4–5·5 produced with glycollic acid. It is stated that 100% wool treated under these conditions is degraded to a negligible extent.

The work on Terylene–wool blends at high temperatures has been planned in the light of work on wool by Lemin *et al.*[31] and Thies[32]. The temperature was restricted to 110–112°c. to minimise degradation of wool, but at this relatively low temperature (for disperse dyes on Terylene) the stain on the wool is no less than that obtained at 100°c. in presence of an efficient carrier: thus the wet fastness is no better, and the only advantage of the high temperature is the elimination of a carrier, which in turn permits a wider choice of disperse dyes having good light fastness. Apart from the Barotor, the only high-temperature piece-dyeing equipment available in the United Kingdom is of the pressurised jig type, and processing Terylene–wool blended fabrics in such equipment may introduce problems in producing fabric having an acceptable handle.

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Discussion

Mr. S. BURGESS: Does the method of application of azoic dyes other than black and navy give good repeats from batch to batch?

Mr. HADFIELD: It has been our experience that the reproducibility is surprisingly good. Azoic dyes are, in general, used only for the production of blacks, navy blues, maroons, and scarlets, and with the azoic combinations recommended no difficulty is encountered with respect to non-reproducibility. It is important, however, that the conditions of application should be the same, particularly the conditions of development with the hot sodium nitrite–hydrochloric acid technique. If reference is made to the work on the effect of development conditions on the tinctorial yield of azoic combinations, it can be seen that the loss of nitrous fumes from the dyeing vessel does affect the tinctorial yield, and therefore changes

in the geometry of the dyeing vessel also will have an effect on reproducibility.

Mr. Burgess: With regard to the daylight fastness of certain disperse dyes on Terylene (Table IV), is any reason known for the anomalous behaviour of those dyes which show decreased fastness at increased depth? Are any such instances known on other fibres, e.g. cellulose secondary acetate or triacetate?

Mr. Hadfield: So far as we are aware, no instances are known where disperse dyes show lower fastness on secondary acetate or triacetate rayon when the depth applied is increased.

Dr. J. Wegmann: I was greatly impressed by the new explanation of the action of carriers, in that additional compounds could be formed which, in spite of a much greater molecular size, diffuse much more rapidly because of inactivation of reactive sites. I do not think that too much importance should be attached to the size of molecules but rather to the substituents determining the character of the molecule. In connection with the azoic technique using 2:3-hydroxy-naphthoic acid, which was shown to give good results on Terylene, it is characteristic that, on nylon, this acid gives relatively poor results compared with its arylamide derivatives. If molecular size were the more important factor, then even better results would be expected with 2:3-hydroxynaphthoic acid combinations on nylon.

Mr. Hadfield: We entirely agree with Dr. Wegmann's comments on the azoic dyeing techniques.

Mr. R. K. Fourness: Have the authors any explanation to offer for the abnormal decrease in light fastness shown by certain disperse dyes on Terylene as the depth of dyeing is increased?

Mr. Hadfield: At this stage we would not like to comment, in detail, on the reasons for the decrease in light fastness when certain disperse dyes are built up to heavy depths on Terylene. Mr. Fourness will know, however, that many disperse dyes which are assumed to be homogeneous are actually mixtures prepared in manufacture, and it may be that a fugitive component is building up in preference to a fast-to-light component.

Dr. C. A. Muhr: What is the best carrier for piece-dyeing wool–Terylene blends from the points of view of the best conditions in the dyebath, easy removal, and minimum effect on the light fastness?

Mr. Hadfield: p-Phenylphenol (Tumescal PH) is the easiest carrier to use for dyeing Terylene–wool blends in piece form. There are no difficulties in using this carrier with respect to dyebath conditions.

Unfortunately, p-phenylphenol reduces the light fastness of certain disperse dyes, particularly reds, and this constitutes a serious drawback to this particular carrier. o-Phenylphenol (Tumescal OP) does not suffer, to the same extent, from reducing the light fastness of dyes, but there are certain difficulties in using this particular carrier for dyeing Terylene–wool mixtures in piece form. These arise from the fact that o-phenylphenol melts at 54°c., and when it melts globules of carrier are sometimes produced in the dyebath which can cause carrier stains. Other techniques have been devised to overcome this difficulty, but the authors have no first-hand information on the practical success of these new techniques. In outline the new techniques involve running a solution of the sodium salt of o-phenylphenol into the buffered dyebath whilst dyeing is being carried out at the boil.

Mr. J. S. Schofield: There are difficulties in heat-setting after dyeing when disperse dyes are used because of their tendency to sublime. The work on azo dyes described in the paper suggests that better fastness can now be obtained in some dark colours by using azoic combinations rather than disperse dyes. Is it likely that this improved fastness will allow us to heat-set after dyeing, which will be a desirable state of affairs if it becomes practicable?

Mr. Hadfield: The increased fastness of azoic dyes to dry heat suggests that it will be practicable to heat-set after dyeing. However, residual intermediates in the fabric can seriously reduce the fastness to sublimation of azoic combinations, and to overcome this difficulty care should be taken that (a) reaction with nitrous acid is as complete as possible and (b) there is an excess of coupling components over base.

Mr. Schofield: Is the Thermosol (DuP) method of dye fixation on Terylene still being followed up, or has the recent progress in dyeing with carriers and in pressure vessels completely superseded it?

Mr. Hadfield: The Thermosol method of dye fixation on Terylene is not, at the moment, being vigorously pursued in this country. The technique is, however, not "dead", and we suspect that one of the reasons why the technique is not being followed up is the small yardage of fabric as yet being piece-dyed. Difficulties in producing a uniform padding over the fabric and also the possibility of seriously contaminating the heat-setting unit are other reasons why this technique is not yet being extensively used. At the present time, in this country, carrier dyeing or dyeing in pressure vessels is the method used to produce the full range of colours on Terylene piece goods.

Dr. G. Schwen: Is there any experience of the Barotor (DuP) machine in this country?

Mr. Hadfield: As far as we are aware, no Barotor dyeing machines are installed in this country, and therefore we have had no first-hand experience.

Chairman — Mr. E. D. POPPER

Bleaching of Nylon and Nylon Blends

S. SHAW and W. S. WILLSON

The effect of chemical bleaching agents on the strength and colour of all-nylon textiles, and on the tensile strength and abrasion resistance of wool–nylon, cotton–nylon, and staple viscose rayon–nylon blended fabrics has been investigated. In addition, methods of bleaching a cotton–nylon blended fabric to give an acceptable white have been described. Removal of heat-setting discoloration from all-nylon material has been discussed, and also the use and misuse of fluorescent brightening agents. The bleaching agents selected for investigation were sodium hypochlorite, hydrogen peroxide, peracetic acid, and sodium chlorite, and details are given of recommended methods of application.

INTRODUCTION

Generally, it is necessary to bleach all-nylon textiles only when they have been yellowed during heat-setting, or to obtain an improved white usually in conjunction with a fluorescent brightening agent. The discoloration caused by heat-setting is due to thermal oxidation of the nylon, and is a function of time at the setting temperature. The extent of the discoloration will determine the severity of the bleaching treatment necessary to remove it, but it should only be slight, otherwise excessive degradation of the fibre may occur. With reference to the colour of nylon yarn as produced, it should be noted that the white appearance depends on the yarn type; semi-dull and fully dull yarn are more opaque and white than the translucent bright yarn.

In some cases, it may be necessary to bleach nylon in order to remove the last traces of identification tints. Although it is important to remove sighting tints by scouring before setting processes, whether dry heat or pressure steam, traces of colour sometimes persist and are then accidentally fixed. In view of this possibility, some anionic dyes have been selected as sighting tints for nylon because they are destructible by an acid sodium chlorite bleach.

The use of nylon staple in blends with cellulosic and protein fibres is becoming increasingly important. Such blends have added wear life over the corresponding all-cotton and all-wool materials and, in some cases, also have increased tensile and rip strength. It is important, therefore, that bleaching processes should not degrade the nylon and destroy these valuable properties. Usually, the nylon content ranges from 10 to 25%, but may be as high as 60–70% when blended with wool for permanent pleating.

Reference has been made to setting: this technique is used to stabilise all-nylon fabrics and to minimise distortion, creasing, and shrinkage during subsequent processes, e.g. scouring, bleaching, and dyeing. Usually, it is not necessary to set blended fabrics unless the percentage of nylon is high, e.g. 50%, and, even so, due consideration must be given to the end-use of the material and the other fibres present. Where experience has shown that rope creases are likely to occur, material containing relatively low percentages of nylon (e.g. 20%) may have to be preset by a method which will not degrade the other fibre. In some cases, open-width processing might be necessary in order to obtain a crease-free result.

The chemicals used for bleaching the natural fibres are oxidising agents, and those in common use are sodium hypochlorite and hydrogen peroxide. The methods of application are firmly established, and it is well known that both products are used for bleaching cellulosic fibres, and that hydrogen peroxide is also used for bleaching protein fibres[1]. The lesser known bleaching agents are sodium chlorite and peracetic acid; they are, however, no longer laboratory curiosities, and their wider use by the trade is being explored.

The investigations described in this paper were designed to determine the effect of these bleaching agents on the strength and the colour of all-nylon textiles; also, to assess the effect of sodium hypochlorite and hydrogen peroxide on cotton–nylon blends and hydrogen peroxide on wool–nylon blends. The nylon fibre used throughout this work was semi-dull 6,6-nylon.

Although the scope of this paper is wide, and therefore not complete in all details, it is hoped that the findings will stimulate further work, and assist processors of nylon and nylon blends to obtain the best possible results.

EXPERIMENTAL

All-nylon Material

SODIUM HYPOCHLORITE

Laboratory Trials on Yarn

Some hanks of 45/15/7½ Z semi-dull yarn were scoured for 30 min. at 185°F. (85°C.) in a solution containing 2 g. of sodium metasilicate and 2 g. of soap per litre, and then thoroughly rinsed and dried.

The hanks were then treated with sodium hypochlorite bleaching liquors at room temperature for 120 min., which was followed by various after-treatments. Details of the treatments and the results of breaking load–extension tests and relative viscosity tests[2,3] on the yarn before and after exposure to sunlight are given in Tables I and II.

TABLE I

Effect of Hypochlorite Bleach Liquors on the Breaking Load-Extension and Relative Viscosity in Formic Acid of 45-denier Nylon Yarn

Sodium Hypochlorite Liquor — Available Chlorine (g./litre)	Bleaching Conditions — pH Initial	Bleaching Conditions — pH Final	Temp. (°C.)	Time (min.)	Antichlor Treatment*	Breaking Load† (g.) Max.	Min.	Mean‡	Extension at Break† (%) Max.	Min.	Mean‡	Relative Viscosity§
0	Control		—	—	—	242	186	218	29·6	16·0	21·1	31·7
1	10·4	10·0	23	120	Nil	244	210	229	28·0	17·2	21·8	29·5
1	10·3	10·2	23	120	NaHSO₃	234	188	225	28·0	14·8	22·6	32·8
1	10·2	10·2	23	120	HCl	224	204	218	28·0	18·4	24·0	31·1
5	10·9	10·5	23	120	Nil	248	230	239	28·4	22·4	25·7	32·1
5	11·0	10·6	23	120	NaHSO₃	250	204	228	29·6	17·2	22·1	32·1
5	10·9	10·9	23	120	HCl	224	180	212	26·8	17·6	21·7	30·3

* NaHSO₃— 2 c.c./litre at room temp. for 10 min.
　HCl— 15 c.c./litre at room temp. for 30 min.

† *Conditions of test—*
　　Constant rate of traverse ... 80 cm./min.
　　Test length ... ... 25 cm.
　　Dry bulb ... ... 77°F.
　　Relative humidity 67%

‡ Control, mean of 60 tests
　Treated samples, mean of 20 tests

§ 8·4% soln. of the yarn in 90% (wt./wt.) formic acid. The relative viscosity is expressed as the ratio of the dynamic viscosity of the solution to the dynamic viscosity of the formic acid solvent. Both viscosities are measured at 25°c. in a No. 3 Ostwald viscometer.

TABLE II

Effect of Exposure to Sunlight on the Breaking Load-Extension of Hypochlorite-bleached 45-denier Nylon Yarn

Sodium Hypochlorite Liquor — Available Chlorine (g./litre)	Bleaching Conditions* — pH Initial	pH Final	Temp. (°C.)	Time (min.)	Antichlor Treatment*	Unexposed† B.L. (g.)‡	Unexposed† B.E. (%)‡	1 month (~160 summer sun hr.)† B.L. (g.)‡	−Δ (B.L.) (%)‡	B.E. (%)‡	−Δ (B.E.) (%)	2 months (~250 summer sun hr.)† B.L. (g.)‡	−Δ (B.L.) (%)‡	B.E. (%)‡	−Δ (B.E.) (%)
0	Control		—	—	—	218	21·1	69	68·3	11·4	46·0	24	89·0	7·3	65·4
5	10·9	10·5	23	120	Nil	242	26·0	100	54·1	12·8	39·3	60	72·5	7·9	62·6
5	11·0	10·6	23	120	NaHSO₃	221	19·5	85	61·0	11·8	44·1	44	79·8	6·4	69·7
5	10·9	10·9	23	120	HCl	217	23·1	58	73·4	8·6	59·3	28	87·2	7·4	64·9

* As for Table I
† Control, mean of 60 tests
　Bleached samples, mean of 10 tests } All exposed samples, mean of 10 tests
‡ B.L. = Breaking load
　B.E. = Extension at break
　Conditions of test as for Table I.

The results indicate that good cotton bleaching practice using alkaline hypochlorite liquors (pH 10–11) containing up to 5 g. available chlorine per litre will not degrade nylon yarn. It would appear that souring with dilute hydrochloric acid after chemicking and rinsing might accelerate the rate of photodegradation of the yarn; also, that bleached yarn with or without subsequent sodium bisulphite antichlor treatment is slightly more resistant to photodegradation than unbleached yarn. In view of the large reduction in strength of the samples after exposure, however, the significance of these results is not known. Visual assessment of colour of bleached and unbleached yarn revealed no improvement in white by bleaching.

In order to investigate the effect of liquor pH and temperature, some additional trials were carried out on similar yarn. The material was scoured as before, and the conditions of treatment and the test results obtained are given in Table III.

The results show that marked degradation of the yarn occurs during bleaching under slightly acidic conditions at approximately 77°F. (25°C.) for a short period of time, e.g. 30 min. On the other hand, bleaching at pH 10·5 at 140°F. (60°C.) causes only a relatively slight reduction in breaking load of the yarn, even over a period of 120 min., but causes an appreciable reduction in extension at break accompanied by some chemical degradation. The latter would indicate that nylon will absorb chlorine from alkaline hypochlorite liquor at high temperatures, the amount absorbed depending upon the concentration–temperature–time factor.

Further trials carried out under slightly acidic conditions at 140°F. (60°C.) resulted in very marked degradation of the yarn and appreciable yellowing.

Works Trial on Fabric

The trials with sodium hypochlorite were taken a stage further by subjecting 20 yd. of a woven all-nylon fabric (continuous-filament warp–staple

TABLE III

Effect of Acidic and Alkaline Hypochlorite Bleaching Conditions on the Breaking Load–Extension and Relative Viscosity in Formic Acid of 45-denier Nylon Yarn

Sodium Hypochlorite Available Chlorine (g./litre)	pH	Bleaching Conditions Liquor Approx. Temp. (°c.)	Time (min.)	Breaking Load* (g.) Max.	Min.	Mean	Extension at Break* (%) Max.	Min.	Mean	Relative Viscosity
0	—	—	—	234	214	223	28·8	20·0	25·7	30·9
2·5	6·6	25	30	158	110	129	16·6	13·0	14·1	21·6
2·5	6·6	25	60	122	100	110	13·8	11·8	12·6	16·5
5·0	6·7	25	30	140	120	126	14·4	12·8	13·8	17·9
5·0	6·7	25	60	124	100	111	14·2	12·0	12·9	13·4
5·0	10·5	60	30	225	200	221	21·4	14·0	16·9	27·6
5·0	10·5	60	60	235	175	225	30·0	17·2	22·4	25·9
5·0	10·5	60	90	224	195	212	18·0	11·2	14·8	25·3
5·0	10·5	60	120	210	190	201	19·0	11·2	14·8	24·7

* Conditions of test as for Tables I and II (30 tests per hank).

weft) to normal cotton piece goods scouring, bleaching, and mercerising processes in a works croft. The material was sewn in with a run of all-cotton fabric.

The trials comprised—

(i) UNTREATED.

(ii) KIER-BOILED— Open boil in rope form for 12 hr. in caustic soda solution (2° Tw.), nylon fabric in centre of kier; rinsed, soured, rinsed, and dried.

(iii) SCOURED AND SET— Scoured in an aqueous solution containing 2 lb. Lissapol N and 2 lb. caustic soda per 100 gal. liquor at 130°F. (55°c.); rinsed and dried.

Set in batch form in pressure steam at 35 lb. per sq. in. for 4·5 min.; material interleaved with cotton wrapper.

(iv) SCOURED, SET, AND KIER-BOILED— As (iii) and boiled as in (ii).

(v) SCOURED, SET, KIER-BOILED, AND MERCERISED— As (iv) plus normal mercerising run; machine set at 37 in. width, 53° Tw. caustic soda solution; fabric rinsed, soured, rinsed, and dried.

(vi) SCOURED, SET, KIER-BOILED, AND BLEACHED— As (iv) plus standard bleach, viz. run wet in cold 1·5° Tw. sodium hypochlorite liquor at pH 10·5–11, piled for 1 hr.; rinsed, sodium bisulphite antichlor treatment, rinsed, and dried.

(vii) SCOURED, SET, KIER-BOILED, BLEACHED, AND MERCERISED— As (vi) and mercerised as in (v).

The fabric was not under width control at any stage except during mercerising and, to a certain extent, during setting.

The results of tests carried out on samples of the material taken at the various stages of processing are given in Table IV.

TABLE IV

Effect of Cotton Piece Goods Scouring, Bleaching, and Mercerising Processes on the Tensile Strength–Extension of a Woven Nylon Cloth

Sample from Process No.	Tensile Strength (lb.)* Before Weathering Warp	Weft	After Weathering† Warp	Weft	Extension at Break (%) Before Weathering Warp	Weft	After Weathering† Warp	Weft	Relative Viscosity Before Weathering	After Weathering†
i	357	235	111	43	30·4	28·5	27·8	16·7	34·9	22·3
ii	Insufficient sample for test		139	66	Insufficient sample for test		34·3	21·9	34·8	26·0
iii	342	236	140	55	35·6	30·9	30·5	20·7	35·8	25·3
iv	362	260	136	79	38·5	36·1	28·6	25·2	35·2	—
v	351	240	262	45	39·0	39·0	30·0	18·1	35·1	21·2
vi	355	215	113	52	31·3	33·7	28·6	23·8	34·5	27·0
vii	324	243	134	63	31·8	33·2	30·9	26·2	33·8	23·7

* Conditions of test—
Denison tensile strength testing machine
Constant rate of traverse   4·5 in./min.
Sample length between jaws 7·0 in.
Sample width   2·0 in.
Averages of   3 tests
Dry bulb   70°F.
Relative humidity   65%
† The approximate number of sun hours during the exposure period was 183.

The tests were carried out on the samples before and after weathering for six weeks on the roof of the Experimental Plant at Pontypool. These results indicate that the various processes cause no marked physical or chemical degradation of the nylon material. Before weathering, the tensile strength of all the samples was of the same order. After weathering, the warp and weft tensile strengths of the processed samples (especially the warp of sample (v) mercerised) were greater than that of the untreated sample. The percentage extension at break, however, of the treated samples, both before and after weathering, was greater than that of the untreated sample, but in all cases the extensions obtained after weathering were lower than those obtained before weathering. The lower extension values may be due to the samples being stretched during exposure, because they were supported between two parallel horizontal wires and were subjected to severe strain by winds.

Under the conditions used during this practical trial, the amount of nylon was very small relative to the amount of cotton present.

HYDROGEN PEROXIDE

Bleaching Methods

The materials were bleached mainly by the basic methods used for the older natural fibres, and the methods investigated were as follows—

ALKALINE STEEP (WOOL)— Material immersed for 16 hr. at 120°F. (50°C.) in 2-vol. hydrogen peroxide containing 4 g. Stabiliser C (Laporte) per litre, liquor pH 9·0–9·2. The material was finally rinsed and dried.

ALKALINE AGE (WOOL)*— Material immersed 20 min. at 120°F. (50°C.) in 4-vol. hydrogen peroxide containing 4 g. Stabiliser C (Laporte) per litre, liquor pH 9·0–9·2. The material was removed from the liquor, and excess solution squeezed out; it was then covered to prevent evaporation and allowed to age for 16 hr. at 120°F. (50°C.). After this treatment the material was rinsed and dried.

ALKALINE AGE DRY-IN (WOOL)— Material immersed for 20 min. at 120°F. (50°C.) in 4-vol. hydrogen peroxide adjusted to pH 9·0–9·5 with sodium silicate (78° Tw.), squeezed, aged for 16 hr. in the damp condition at 120°F. (50°C.), and dried without rinsing.

ACID AGE (WOOL)*—Material immersed for 20 min. at room temperature in 4-vol. hydrogen peroxide adjusted to pH 4·5 by the addition of formic acid. The material was then removed, squeezed, aged for 16 hr. at room temperature, rinsed, and dried.

ACID AGE DRY-IN (WOOL)*†— Material immersed for 20 min. at 120°F. (50°C.) in 4-vol. hydrogen peroxide adjusted to pH 4·5 by the addition of oxalic acid and sodium pyrophosphate in the ratio of 0·9 g. oxalic acid per litre to 1·6 g. sodium pyrophosphate per litre. The material was

removed from the liquor, and excess solution removed by squeezing. The material was then aged for 16 hr. in the damp condition at room temperature and dried without rinsing.

ACID AGE DRY-IN (WOOL)‡— Material immersed for 20 min. at room temperature in 4-vol. hydrogen peroxide containing 2 c.c. formic acid (85%) per litre and adjusted to pH 3·5 with sodium carbonate, removed, squeezed, aged for 16 hr. at room temperature, and dried without rinsing.

STABILISER MP DRY-IN (WOOL)— Material immersed for 20 min. at 100°F. (38°C.) in 4-vol. hydrogen peroxide and 3 g. Stabiliser MP (Laporte) per litre at pH 4·0, squeezed, aged by standing for 16 hr. in the damp condition, and dried without rinsing.

SCOUR AND BLEACH (COTTON)—Scoured— Boiled for 3 hr. in a solution of sodium hydroxide (5% on weight of material). Rinsed, hot and cold water.

Bleached— Boiled for 6 hr. in a solution comprising—

0·5-vol. hydrogen peroxide
12·0 g. sodium silicate (78° Tw.) per litre ⎱ pH ca. 11·0
0·05 g. sodium hydroxide per litre ⎰

The material was finally rinsed in hot and cold water before drying.

SCOUR AND BLEACH (COTTON–VISCOSE RAYON) —Scoured— Scoured for 2 hr. at 180–190°F. (82–88°C.) in a solution comprising—

2·0 g. soda ash
2·0 g. sodium chloride per litre
2·0 g. Linol (Laporte)—a built detergent of sulphated fatty alcohol type

Rinsed, hot and cold water.

Bleached— Treated for 2½ hr. at 180–190°F. (82–88°C.) in a solution comprising—

0·5-vol. hydrogen peroxide
7·0 g. sodium silicate (78° Tw.) per litre ⎱ pH ca. 11·0
0·4 g. sodium hydroxide per litre ⎰

The material was finally rinsed in hot and cold water and dried.

Except where otherwise stated, all the material was prescoured for 30 min. at 140°F. (60°C.) in a solution containing 3 g. soap flakes and 1 c.c. ammonia (sp. gr. 0·88) per litre, and all the treatments were carried out at a liquor : material ratio of 20 : 1. It is believed that the methods marked with an asterisk (*) are not in use commercially.

Results of Laboratory Trials on Yarn and Fabric

In general, it was found that the cotton and cotton–viscose rayon bleaching methods, which are applied at high pH and high temperature, cause very marked reduction in tensile strength of the nylon; in the case of fabric, this drop in strength was not accompanied by a corresponding change in relative viscosity. The alkaline wool bleaching

TABLE V

Effect of Hydrogen Peroxide Bleaching Treatments on the Strength of Woven Nylon Cloth before and after Exposure in a Fugitometer

Method of Bleaching	Unexposed										Exposed for 50 hr. in Fugitometer (water jacket removed)									
	Treated Samples						Controls (Untreated)					Treated Samples						Controls (Untreated)			
	Warp		Weft				Warp		Weft			Warp		Weft				Warp		Weft		
	B.L. (lb.)*	B.E. (%)*	B.L. (lb.)*	B.E. (%)*	Relative Viscosity		B.L. (lb.)	B.E. (%)	B.L. (lb.)	B.E. (%)	Relative Viscosity	B.L. (lb.)	B.E. (%)	B.L. (lb.)	B.E. (%)	Relative Viscosity		B.L. (lb.)	B.E. (%)	B.L. (lb.)	B.E. (%)	Relative Viscosity
Alkaline steep (wool)	51·1	22·2	46·2	22·2	32·6							36·8	13·1	30·6	17·1	23·8		29·6	12·1	25·6	15·0	**
Blank	100·0	24·4	93·8	31·1	31·8							46·2	13·3	27·6	16·4	21·8						
Alkaline age (wool)	51·9	17·8	56·1	22·2	30·8							40·4	13·8	34·2	18·1	23·7		54·7	18·2	49·1	22·1	23·5
Blank	97·4	35·6	91·2	31·1	31·6							60·3	18·6	46·8	21·4	23·2						
Acid age dry-in (wool)†	92·4	22·2	91·5	35·6	30·3		101·0	30·0	94·0	31·1	32·6	40·0	16·4	34·6	18·3	21·3		40·9	14·3	30·1	16·1	**
Blank	96·8	24·4	95·2	31·1	31·4							44·0	14·8	37·4	17·9	21·7						
Acid age (wool)‡	86·8	22·2	93·1	31·1	30·9							37·1	14·3	30·2	16·2	22·6		24·2	11·1	20·7	12·0	21·6
Blank	89·8	26·7	96·2	33·3	31·4							31·2	11·4	30·6	18·6	22·2						
Cotton	18·4	22·2	26·0	17·8	28·3							12·1	7·4	17·0	13·8	20·4		44·7	15·7	36·1	16·1	21·0
Blank	100·1	28·9	101·2	37·8	31·8							57·9	20·0	59·8	24·1	25·0						

* B.L. = Breaking load
  B.E. = Extension at break
  Conditions of test as for Table IV

† Oxalic acid–pyrophosphate
‡ Formic acid
** Insufficient material for individual tests; average result = 21·8.

methods also cause a severe reduction in strength, approximating to 50%. On the other hand, the acid wool bleaching methods—particularly the oxalic acid–sodium pyrophosphate mixture and Stabiliser MP methods—were found to cause only slight loss in strength under ideal bleach-bath conditions. One sample, however, bleached by the acid age dry-in method (oxalic acid–sodium pyrophosphate mixture) showed an appreciable decrease in breaking load, about 45% in warp and 25% in weft. The reason for this low result was not known, especially as a repeat bleaching trial resulted in little or no decrease in strength. It was thought that the degradation which had occurred might be due to catalytic decomposition of the hydrogen peroxide by contaminating metals in the bleach liquor, e.g. iron from the stabilisers used [4].

Visually, there appeared to be a slight improvement in colour in all cases over the unbleached material, but no distinguishable difference between the bleached samples.

In order to separate the effect upon nylon of hydrogen peroxide and of the other agents involved, it was decided to repeat some of the basic bleachings and include a set of blank baths omitting the hydrogen peroxide. In addition, light exposure tests were carried out. The results of these experiments on nylon fabric are given in Table V.

The results show that the oxidising conditions, not the other bleach-bath conditions, were the cause of loss of strength.

There are some anomalies in the results obtained after exposure to light as shown by the controls. They are probably associated with experimental conditions, since each set of bleached samples, along with corresponding blanks and controls, had to be exposed separately because of the limited capacity of the Fugitometer. These results indicate, however, that the bleaching processes have not accelerated the photodegradation of the yarn.

The cotton and cotton–viscose rayon methods were repeated on some two-fold 45-denier yarn, and although a severe reduction in tensile strength occurred, it was not so marked as on the samples of fabric. Also, the reduction in relative viscosity appeared to be more in line with the loss in tensile strength. The results obtained are given in Table VI.

TABLE VI

Effect of Cotton and Cotton–Viscose Rayon Hydrogen Peroxide Bleaching Treatments on the Strength of 2/45-denier Nylon Yarn*

Method of Bleaching	Breaking Load (g.)	Extension at Break (%)	Relative Viscosity
Scoured only	402·6	21·7	29·0
Cotton	162·4	11·0	22·2
Cotton–viscose rayon ...	238·8	14·7	23·5

* *Conditions of Test*—
  Uster constant-rate-of-load machine
  3 tests per min.
  Means of 200 tests
  Temp. 69°F.
  R.H. 67%.

PERACETIC ACID

Application

It was found that this chemical will improve the natural whiteness of nylon yarn as manufactured, and also remove heat-setting discoloration. The recommended recipe is as follows—

Peracetic acid (40%) ... ... 3 lb. per 100 gal. water (normally 1–5 lb./100 gal.)

*Anhydrous sodium pyrophosphate ... ... 0·25 lb. per 100 gal.

Wetting agent ... ... 1 lb. per 100 gal.

pH of solution (adjusted with caustic soda, about 0·5–0·75 lb. per 100 gal.) ... 6–7

Liquor : goods ratio ... ... 20 : 1

Processing temperature and time ... ... Temperature raised to 175–185°F. (80–85°C.) in 30 min. and then maintained for 30 min.

* Sodium pyrophosphate may be replaced by sodium hexametaphosphate, which creates the most stable conditions. It is recommended where conditions of operation are not ideal, owing to possible bleach-bath contamination. The amount of sodium hexametaphosphate to use is 0·5 lb. per 100 gal. of water.

The bleaching process is followed by thoroughly rinsing the fabric before drying in the usual way.

The bleaching operation can be carried out in stainless-steel equipment of the conventional type, but copper, brass, and iron should be strictly avoided. Metals such as maganese, iron, copper, and their salts cause catalytic decomposition of peracetic acid, and therefore care should be taken to ensure that it does not become contaminated. However, when stored in a cool place in a vented container, it is claimed by the manufacturers that peracetic acid will substantially maintain its strength for three months. Provided that adequate precautions are taken in handling this chemical, no troubles should arise [5].

Laboratory Trials on Yarn and Fabric

The effect of concentration and pH of peracetic acid bleaching liquor was investigated on monofil yarn and also on locknit fabric constructed from multifil yarn. The conditions of bleaching and test results obtained on conditioned fabric are given in Tables VII and VIIA.

TABLE VII

Effect of Concentration and pH of Peracetic Acid Bleaching Treatments on the Strength of 15-denier Monofil Nylon Yarn*

Conditions of Bleaching	Breaking Load (g.)	Extension at Break (%)
Control (scoured only)	97·9	31·3
3 g./litre, pH 7·0	91·0	27·0
6 g./litre, pH 6·8	90·9	26·5
10 g./litre, pH 7·0	85·4	23·7
20 g./litre, pH 6·8	85·0	27·3
Control (scoured only)	96·8	41·6
3 g./litre, pH 5·4	84·2	24·4
6 g./litre, pH 4·5	91·0	30·2

* Initial concentration of peracetic acid = 40%
0·25 g. sodium pyrophosphate per litre in bleach bath
pH adjusted with caustic soda where necessary
Averages of 20 tests on constant-rate-of-traverse serimeter.

The breaking load results on the yarn indicate that the recommended bleaching procedure using 3 g. peracetic acid per litre does not cause an undue reduction in strength of the yarn. On the other hand, increasing the peracetic acid concentration to 10 g./litre results in about 13·0% reduction in strength. The extensibility results were not reproducible on different samples treated similarly.

The test results on fabric do not readily differentiate between the various bleaching conditions. On unset material the greatest decrease in strength (14·5%) occurred at pH 4.

On set material, all the treatments resulted in a somewhat similar decrease in strength of the fabric, the greatest being ca. 10% caused by the recommended bleaching method. This figure is additional to the 7% decrease caused by setting.

The decomposition of the bleaching solutions used in the trial on fabric was determined [6], and it was found that the free hydrogen peroxide content remained fairly constant in each case (Table VIII).

TABLE VIIA

Effect of Concentration and pH of Peracetic Acid Bleaching Treatments on Strength of Nylon Locknit Fabric

Conditions of Bleaching*		Unset		Set	
Concn. (g./litre)	pH	Average Bursting Strength (lb./sq. in.)†	Relative Viscosity	Average Bursting Strength (lb./sq. in.)†	Relative Viscosity
Not bleached		132	32·1	123	29·9
1	6·0–7·0	117	30·8	114	28·8
3	6·0–7·0	123	31·4	111	29·1
6	6·0–7·0	127	31·3	114	28·4
10	6·0–7·0	125	31·1	116	28·8
3	4·0	113	30·6	112	28·7
3	8·5	120	31·3	112	28·9

* Initial concn. of peracetic acid = 40%
Sodium hexametaphosphate (0·5 g./litre) in bleach bath
pH adjusted with NaOH where necessary
Temp. raised to 180°F. (82°C.) in 30 min., and maintained for 30 min.
Liquor ratio 20 : 1
† Mullen machine, 1 in. diameter. Averages of 10 tests

TABLE VIII

Decomposition of Peracetic Acid Solutions during Bleaching

Initial Concn. (g./litre)	Approx. pH	Free H_2O_2 (vol.) Start	Finish	CH_3·COOOH (g./litre) Start	Finish	pH Start	Finish
1	6·0–7·0	0·03	0·05	1·3	1·2	6·2	6·0
3	6·0–7·0	0·08	0·08	3·4	2·3	5·8	5·6
6	6·0–7·0	0·14	0·16	6·5	3·7	6·1	5·5
10	6·0–7·0	0·26	0·31	10·7	6·6	5·9	5·3
3	4·0	0·08	0·08	3·6	2·6	4·3	4·0
3	8·5	0·05	0·05	3·5	3·1	8·6	8·4

Works Trials on Fabric

As far as can be ascertained in the United Kingdom, trade experience seems to confirm that peracetic acid is a safe bleach for nylon. In the early stages, however, the results of tests carried out on two B.N.S. experimental warp-knitted fabrics which had been bleached in the trade with peracetic acid indicated a loss in strength of 20–30% caused by the peracetic acid bleach. There was some doubt about the validity of these results, since the work was carried out during the introduction of peracetic acid in this country, and the possibility of bleach-bath contamination cannot be ruled out.

The matter was reported to Laporte Chemicals Ltd., who carried out an additional works trial. Samples of 30-denier warp-knitted fabric were taken from a peracetic acid user where the method had been introduced by Laporte technical staff and reasonable control maintained on the bleaching process. The samples were taken from a standard production run, and were subsequently tested for bursting strength by the Manchester Chamber of Commerce Testing House. The results obtained are given in Table IX.

TABLE IX

Effect of a Works Peracetic Acid Bleaching Process on the Bursting Strength of 30-denier Nylon Warp-knitted Fabric*

Test Method	Un-set	Set	Set and Bleached commercially	Unset and Bleached (laboratory)†
Bursting strength, lb./sq. in. ...	128	101	102	124
Fluidity numbers (m-cresol) ...	17·1	19·8	17·2	15·2

* Mullen machine, 1000 lb./sq. in. capacity
  Averages of 20 tests
† Bleached in laboratory by standard method.

The results show that the commercial bleaching method has not caused any damage additional to that caused by setting; it is our opinion, however, that the decrease in strength due to setting (21%) is excessive. The laboratory bleaching treatment caused very little decrease in strength of the unset material.

SODIUM CHLORITE

In this country, it is true to say that there is more experience in the use of sodium chlorite than peracetic acid, no doubt owing to the former being the first on the market as a practical bleaching

proposition. This experience has largely been gained with nylon fabrics, both warp knits and woven, as a bleach to remove discoloration after setting; sodium chlorite will also improve the white appearance of the yarn.

Application

A standard bleach recipe for application to nylon textiles is as follows—

Sodium chlorite (80% concn.) ...	Up to 3 lb. sodium chlorite per 100 gal. of water (or 3 g./litre)
pH solution (e.g. adjusted with acetic or formic acid) ...	3–5
Liquor : goods ratio	20–40 : 1
Processing time and temperature	30 min. at 185°F. (85°C.)

To stabilise the pH, additions may be made to the bleaching bath of tetrasodium pyrophosphate ($\frac{1}{2}$–1 lb. per 100 gal. of liquor), and a small proportion of a synthetic detergent, stable under acid conditions, may be added to assist in the bleaching action.

The bleaching process is followed by neutralising the material in dilute sodium carbonate solution and then thoroughly rinsing in water.

Laboratory Trials on Yarn

Much experimental work has been done in this field both by the manufacturers of the chemical and by other investigators, and the fact that sodium chlorite used in acid solutions is a safe bleach for nylon is well established [7–9]. The following test results on monofil and multifil yarn (Tables X and XA) are typical and show that strength is unimpaired by bleaching.

TABLE X

Effect of Sodium Chlorite Bleaching Treatments on the Strength of 15-denier Monofil Nylon Yarn*

Sodium Chlorite (80%) (g./litre)	pH of Bleach Liquor†	Breaking Load (g.)	Extension at Break (%)
0 (control)	—	92·8	26·8
1·0	4·0	94·7	31·4
3·0	4·0	94·3	32·4

* Bleaching temp. and time = 85°c. for 30 min.
  Averages of 20 tests on constant-rate-of-traverse serimeter
† Adjusted with acetic acid.

The tenacity of bleached 45-denier yarn was tested after exposure for 50 hr. in a Fugitometer and also after storage for 6 months in the dark. The results indicated that the acid sodium chlorite treatment had virtually no detrimental effect.

TABLE Xₐ

Effect of Sodium Chlorite Bleaching Treatment on the Tenacity of 45/15/7½S Type-100 Nylon Yarn*

Sodium Chlorite (80%) (g./litre)	pH of Bleach Liquor†	Temp. (°C.)	Time (min.)	Yarn tenacity (g./denier)
0 (control)	—	—	—	5·0
0·5	4·2	85	30	5·0
1·5	4·3	85	30	4·9
3	4·3	85	30	4·9

* Averages of 30 tests on constant-rate-of-traverse serimeter.
† Adjusted with formic acid.

Corrosion of Metal Equipment

Acid solutions of sodium chlorite attack metal, including stainless-steel, vessels. If the metal is attacked, there is a risk of damage to the nylon by catalytic action and, in addition, rough places on the metal will cause snags. The chemical manufacturers, therefore, recommend the use of either earthenware or wooden vessels to hold the bleach liquor.

Methods of reducing the rate of corrosion and even eliminating it have been suggested. For example, commercial inhibitors are available for inclusion in the bleach bath: the *modus operandi* of these auxiliaries is to control the development of chlorine dioxide so that theoretically it is used as it is formed. This promotes more efficient and economic bleaching and reduces fuming, the latter effect being due partly to the stabilising action of these agents and, in some cases, also to a layer of foam which is formed on the surface of the liquor.

The inclusion of inorganic salts such as sodium nitrate (1–2 g./litre) in the bleach bath gives some protective effect. Furthermore, it is believed that the use of nitric acid or oxalic acid for acidifying the bath has also been suggested as a means of reducing the rate of corrosion.

In addition to these agents, there is a brand of sodium chlorite on the market which contains a corrosion inhibitor, and trade experience indicates that this product is satisfactory in use.

Metal vessels can be made corrosion-resistant by polarisation [10]. It is stated that the metal of the vessel may be polarised by either of the following methods—

(i) By means of a source of electrical energy

(ii) By introducing into the acid chlorite solution a protecting metal which is more electropositive than the metal of the receptacle and in addition makes electrical contact between the two metals.

Generally speaking, stainless steels containing molybdenum are somewhat more resistant to attack than those without. Unpolished surfaces and welds are the most vulnerable. Some scouting trials were carried out using 5-g./litre sodium chlorite solutions (initial concentration) at 80–85°C. for 100 hr., baths being changed about every 6–8 hr. The results indicated the effectiveness of corrosion inhibitors in the bleach bath. However, in one series of tests the welds were attacked, and this was discussed with the machinery maker who had supplied the small test samples. It was thought to be due to the welds being contaminated with small particles of metal which had not been removed during the final smoothing operation.

For further information on the corrosion resistance of various materials to sodium chlorite bleaching solutions, the reader is referred to a detailed investigation which has been carried out by J. Meybeck *et al.*[11–14].

Suppression of Fumes

When acid solutions of sodium chlorite are used, the presence of free chlorine dioxide may sometimes be found to be objectionable to personnel. In addition, it is also necessary to prevent free chlorine dioxide from coming into contact with dyed goods and affecting the colour. It has been suggested that hydrogen peroxide can be used to reduce chlorine dioxide to chlorous acid [15]—

$$2\ ClO_2 + H_2O_2 = 2\ HClO_2 + O_2$$

It has been found that the addition of hydrogen peroxide to sodium chlorite solutions does not impair their bleaching efficiency, and that 1 pint of 100-vol. hydrogen peroxide per 100 gal. of sodium chlorite solution should prevent the evolution of free chlorine dioxide gas.

As already mentioned, however, some proprietary corrosion inhibitors will suppress fumes, and in some cases buffer the bleach bath.

It has also been claimed that improved bleaching action may be obtained, and the consumption of chlorite materially reduced, by the selection of certain fluoride compounds for use in the bath [16]. The loss of chlorine dioxide is held within reasonable limits, and the gas is used up almost entirely by the material to be bleached, without substantial discharge into the atmosphere. The addition of phosphorus derivatives, either in the form of their free acids or in combined form as mono-, hexa-, or poly-phosphates, is also stated to be advantageous.

Precautions recommended when handling Sodium Chlorite

Sodium chlorite should be kept dry during storage. It should be handled with clean dry scoops and never with any material containing sulphur, since this causes spontaneous combustion, especially in the presence of moisture. Small

traces of sodium hydrosulphite have been known to cause a ladle of sodium chlorite to burst into flames.

In general, the precautions taken when handling sodium chlorate should be observed with the chlorite, e.g. keeping it away from easily combustible material.

FLUORESCENT BRIGHTENING AGENTS

There are a number of fluorescent brighteners on the market which can be applied to nylon, some from an acid bath, others from a neutral bath. It is well known that these agents possess a characteristic fluorescence, usually pink or greenish blue; they have the property of absorbing ultraviolet radiation and then transmitting it as visible light, improving the brightness of white or dyed material.

The light fastness and the washing fastness of these agents on nylon range from poor to moderate, but it is believed that the latest products have improved fastness properties. In general, however, exposure to light and repeated washing soon lead to deterioration in whiteness. On the other hand, it is known that some domestic detergents contain fluorescent brighteners which have affinity for nylon, and therefore help to maintain the white.

When used in nylon finishing, fluorescent brightening agents should be applied only to material which has not been discoloured during processing, or to chemically bleached material. If they are used to cover up very slight discoloration, their removal under either end-use or display conditions will unmask the discoloration. In addition, overloading the fabric with these agents should be avoided, as it imparts an objectionable colour-cast to the material: the minimum amount compatible with a good white is all that is required. Some of these agents can be applied in the chemical bleach baths [17], making the process a one-bath as against a two-bath method.

REMOVAL OF DISCOLORATION FROM HEAT-SET MATERIAL

Our investigations have shown that both peracetic acid and acid solutions of sodium chlorite will satisfactorily remove thermal oxidative discoloration from nylon.

The conditions of bleaching are as previously described in this paper. The quantity of bleaching agent required will vary according to the degree of discoloration, but sodium chlorite concentrations of 0·5–1 g./litre and a 0·3% solution of peracetic acid should be adequate [18, 19].

In the case of goods containing coloured effects, usually dyed with anionic dyes, discoloured ground material can be cleared using peracetic acid and a modified bleaching technique. The minimum amount of bleaching agent should be used, and the temperature not raised above 149°F. (65°C.) in order that the dyed effects may remain relatively

unchanged. It is recommended that processers test samples of the coloured effects for fastness to this process before proceeding in bulk. Sodium chlorite cannot generally be used for this process, because it is a highly efficient dye-stripping agent. There are indications that acid hydrogen peroxide bleaching processes might be useful for removing very slight discoloration from material containing dyed effects. In general, however, hydrogen peroxide is not satisfactory for removing heat-setting discoloration. The yellowness of heat-set nylon should not be confused with the discoloration which sometimes occurs during wear and which cannot be chemically bleached. Thermal oxidative yellowing is destroyed by exposure to sunlight and to the carbon arc as well as by chemical bleaching.

Blends

WOOL–NYLON

Hydrogen Peroxide

(laboratory trials on fabric)

Although the alkaline peroxide wool-bleaching methods had been found to cause appreciable degradation of nylon when applied to all-nylon material, trade experience indicated that these methods could be safely applied to wool–nylon blends.

It was decided, therefore, to investigate the matter on a laboratory scale in order to ascertain if the wool exerted a protective effect on the nylon in the blend. A sample of 90 : 10 wool–nylon fabric was bleached using the alkaline steep and alkaline age processes, and also the Stabiliser MP method, which was included as a control acid process. In addition, samples of all-wool fabric were bleached along with those of the wool–nylon blended fabric as a further check on the bleaching processes.

The various samples were tested for tensile strength and abrasion resistance, and the results obtained are given in Table XI.

None of the methods reduced the abrasion resistance of the fabrics significantly. With the high coefficient of variation it would appear that there is little or no difference in the sets of abrasion resistance results for each fabric with the exception of the acid Stabiliser MP method, which gave higher results. This method also appears to have resulted in increased tensile strength of both fabrics.

From these laboratory results it would appear that the normal alkaline hydrogen peroxide bleaching processes used for wool are probably safe when applied to a blend containing a low percentage of nylon. In the case of blends containing a major proportion of nylon, however, the results of the bleaching trials on all-nylon material indicate that it would be advisable to bleach by the acid hydrogen peroxide method.

TABLE XI

Effect of Hydrogen Peroxide Bleaching Processes on Tensile Strength and Abrasion Resistance of All-wool and Wool-Nylon (90 : 10) Cloths

Method of Bleaching	Tensile Strength (lb.)*		Elongation at Break (%)		Abrasion Resistance†			
	Warp	Weft	Warp	Weft	No. of Rubs to Hole	v‡ (%)	Loss in Wt. (%)§	v (%)
			WOOL, SCOURED**					
—	62·0	46·0	36·4	31·4	3662	24·5	9·3	33·4
Alkaline steep ...	61·8	47·0	40·1	30·9	4566	52·4	10·0	15·1
Alkaline age ...	61·8	46·6	40·4	30·9	3224	28·1	8·9	31·6
Alkaline age dry-in	63·6	46·5	40·4	31·6	3541	55·9	9·6	39·5
Stabiliser MP ...	67·8	51·8	41·5	37·0	7493	59·3	8·3	31·8
			WOOL-NYLON, SCOURED**					
—	53·5	55·6	33·0	37·1	4550	38·6	9·5	45·6
Alkaline steep ...	50·0	49·0	31·6	33·2	5273	43·3	6·6	14·2
Alkaline age ...	50·8	53·1	32·0	33·2	6088	43·1	5·9	21·4
Alkaline age dry-in	54·0	60·0	33·2	37·3	5737	48·2	6·8	25·1
Stabiliser MP ...	58·0	63·5	36·1	38·9	8258	42·8	8·0	42·6

* Conditions of test as for Table IV
† Martindale machine, grade 0 emery cloth. Averages of 10 tests
‡ v = Coefficient of variance
§ At the recorded number of rubs to hole
**Before bleaching, both lengths of fabric were scoured together under the following conditions—
   (i) 4 g. Linol + 2 g. soda ash + 4 g. salt per litre— run for 15–20 min. at 120°F. (50°C.) on winch machine; squeezed.
   (ii) 2 g. Linol + 2 g. salt per litre— run for 15–20 min. at 110–115°F. (ca. 45°c.); rinsed in warm and cold water, squeezed, and hydro-extracted.

COTTON–NYLON

Hydrogen Peroxide

(laboratory trials on fabric)

The cotton and cotton–viscose rayon bleaching methods which had been found to degrade markedly all-nylon material were applied to a 75 : 25 cotton–nylon blended fabric. Included in the bleaching trial was a length of an all-cotton fabric which was similar, but not identical in construction, to the blend.

The results of tensile strength and abrasion resistance tests on the fabrics before and after bleaching are given in Table XII.

It is shown that the bleaching processes have not impaired the strengths of the fabrics. The high coefficients of variation in the sets of abrasion resistance results indicate that there are no significant differences within the all-cotton, nor within the cotton–nylon, results.

These laboratory results indicate that the hydrogen peroxide bleaching processes normally applied to cotton and cotton–viscose rayon mixtures are probably safe for the bleaching of cotton–nylon blended material containing up to 25% nylon, the cotton presumably protecting the nylon.

TABLE XII

Effect of Hydrogen Peroxide Bleaching Processes on Tensile Strength and Abrasion Resistance of All-cotton and Cotton–Nylon (75 : 25) Cloths

Method of Treatment	Tensile Strength (lb.)*		Elongation at Break (%)		Abrasion Resistance†			
	Warp	Weft	Warp	Weft	No. of Rubs to Hole	v‡ (%)	Loss in Wt. (%)§	v (%)
			COTTON					
Scoured**	239·5	172·6	29·9	10·0	5303	28·2	3·4	23·2
Scoured and bleached**	260·0	183·3	26·7	10·2	4382	33·6	3·2	39·6
Scoured††	277·5	170·4	32·5	9·8	3748	37·8	1·9	47·8
Scoured and bleached††	217·8	173·3	26·2	9·3	4686	32·0	2·8	41·2
			COTTON–NYLON					
Scoured**	224·3	118·5	25·3	10·0	7603	20·6	2·7	18·3
Scoured and bleached**	226·6	129·3	26·7	9·3	7394	10·1	2·7	17·7
Scoured††	251·0	127·0	28·9	11·1	6184	26·4	2·4	18·3
Scoured and bleached††	236·5	121·7	28·6	10·4	7266	21·7	3·7	26·6

* Conditions of test as for Table IV
† Conditions of test as for Table XI
‡ v = Coefficient of variance
§ See Table XI
**Before bleaching by the cotton method, the respective fabrics were scoured together in caustic soda at the boil.
††Before bleaching by the cotton–viscose rayon method, the respective fabrics were scoured together in soda ash, common salt, and Linol at 180–190°F. (82–88°c.) (see p. 860).

TABLE XIII
Analysis of Loom-state and Finished Fabrics

Fabric (plain weave)	All-cotton		Cotton–Nylon		All-Fibro		Fibro–Nylon	
	Grey	Finished	Grey	Finished	Grey	Finished	Grey	Finished
Ends/in.	74	80	76	81	76	83	77	81
Picks/in.	59	58	59	58	57	55	58	59
Weight, oz./sq. yd....	5·3	4·8	5·3	4·9	5·1	5·9	5·3	5·7
Cotton counts—								
Warp	18·6	22·0	20·8	22·2	19·5	18·2	19·2	18·3
Weft	19·9	21·2	17·7	21·7	21·5	17·2	19·8	18·4

Sodium Hypochlorite
(works trials on fabric)

The fabrics selected comprised the following—

All-cotton
Cotton–nylon (80 : 20 cotton–nylon in warp and weft)
All-Fibro (Courtaulds)
Fibro–nylon (80 : 20 Fibro–nylon in warp and weft)

and were processed as follows—

COTTON AND COTTON–NYLON— Desized in enzyme; pressure-boiled at 20 lb./sq. in. for 8 hr. in caustic soda solution; bleached in ¼° Tw. sodium hypochlorite liquor and rinsed; soured in dilute sulphuric acid and rinsed; scutched and mangled; mercerised and cylinder-dried.

FIBRO AND FIBRO–NYLON— Desized in enzyme; low-pressure-boiled for 4 hr. in solution of Lissapol N and soda ash; bleached in ¼° Tw. sodium hypochlorite liquor and rinsed; soured in dilute sulphuric acid and rinsed; scutched and mangled; cylinder-dried; anti-crease-finished by normal process for Tebilised (T.B.L.) goods.

Samples for testing were taken at the following stages of processing—

Stage	Cotton and Cotton–Nylon Fabrics	Fibro and Fibro–Nylon Fabrics
i	Loom-state	Loom-state
ii	After high-pressure boil	After low-pressure boil
iii	After bleaching and rinsing	After bleaching and rinsing
iv	After souring and rinsing	After souring and rinsing
v	Finished	Finished

Test Results

The results of analysis of loom-state and finished fabrics are given in Table XIII.

Abrasion resistance and tensile strength tests were carried out on randomly selected areas of each sample. Patterns (7 in. square) were cut out and tested as follows—

(a) Abraded to hole
(b) Abraded to 500 rubs and then tested for tensile strength
(c) Abraded to 1,000 rubs and then tested for tensile strength
(d) Abraded to 1,500 rubs and then tested for tensile strength
(e) Abraded to 2,000 rubs and then tested for tensile strength
(f) Abraded to 3,000 rubs and then tested for tensile strength.

ABRADED TO HOLE (a)— A Martindale machine was used for the abrasion resistance tests with the pattern in the bottom position, and the abradant was grade 0 emery paper. The results obtained are given in Table XIV.

These results show that there is an improvement in abrasion resistance with the inclusion of nylon in both the cotton and Fibro fabrics, and this improvement is more than maintained throughout all the processes. The abrasion resistance of the all-cotton and all-Fibro fabrics has been reduced about 42% and 29%, respectively, by the full bleaching and finishing processes, whereas that of the cotton–nylon and Fibro–nylon has not decreased, as summarised in Table XV.

ABRASION–TENSILE STRENGTH (b)–(f)— The abraded samples were tested on a Denison strength-testing machine in a conditioned atmosphere; distance between the jaws 3 in., strips 2 in. wide; constant rate of traverse 4½ in./min. The average results obtained (5–8 tests) are given graphically in Fig. 1–3, which show the superiority of the nylon blends over the all-cotton and all-Fibro counterparts.

TABLE XIV
Abrasion Resistance of Fabrics at Various Stages of Bleaching

Stage	All-cotton*		Cotton–Nylon†		All-Fibro‡		Fibro–Nylon§	
	No. of Rubs to Hole	v (%)	No. of Rubs to Hole	v (%)	No. of Rubs to Hole	v (%)	No. of Rubs to Hole	v (%)
(i)	3593	31·8	4507	36·5	2416	29·2	3478	20·4
(ii)	2397	18·7	5733	24·6	1998	25·3	4095	24·3
(iii)	2192	22·6	4996	20·3	1718	19·7	4806	17·9
(iv)	2352	26·4	4968	26·1	2099	25·0	3950	28·6
(v)	2107	26·8	4415	17·3	1666	31·9	4005	27·7

* Averages of 12 tests
† Averages of 10 tests–8 tests (i)
‡ Averages of 12 tests–11 tests (ii)
§ Averages of 11 tests–7 tests (i)
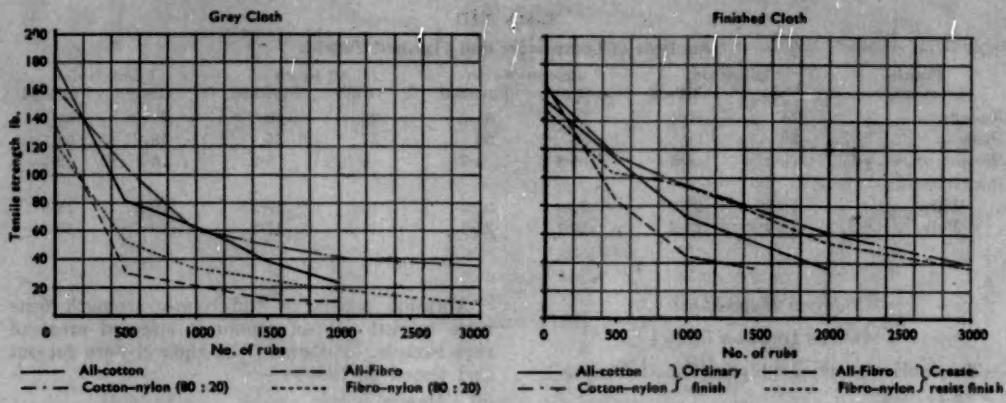
FIG. 1
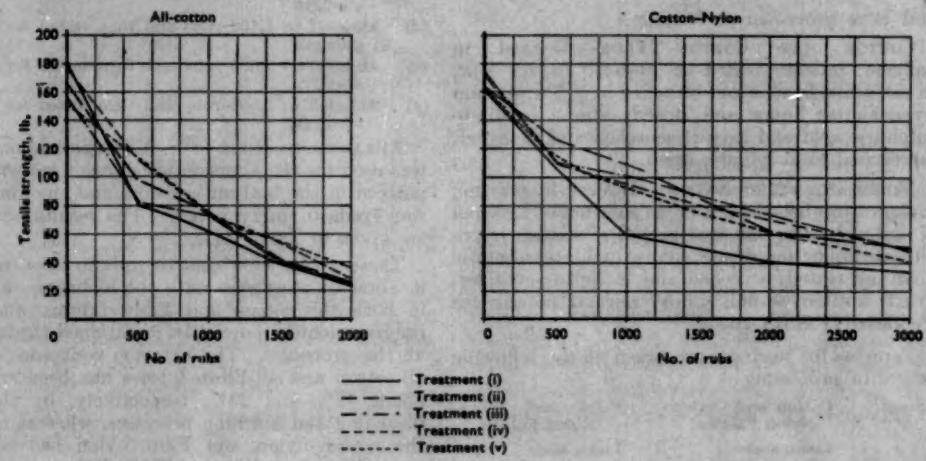
FIG. 2
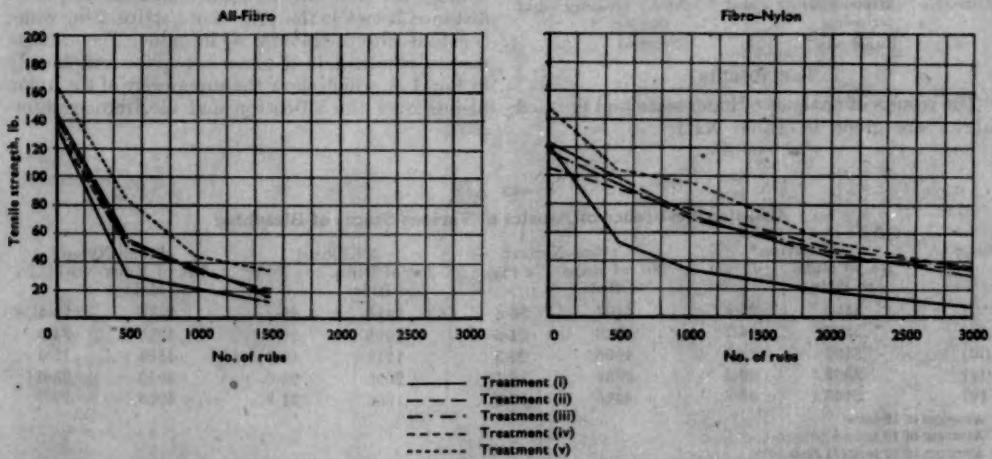
FIG. 3

TABLE XV

Abrasion Resistance of Grey and Finished Fabric

(rubs to hole)

	All-cotton	Cotton–Nylon	All-Fibro	Fibro–Nylon
Grey fabric ...	3593	4507	2416	3478
Finished fabric ...	2107	4415	1666	4005
Loss (approx.), %	42	2	29	−14 (increase)

Methods of Bleaching to give an Acceptable White

It had been drawn to our attention by the trade and was also confirmed by our trials on yarn and fabric that the colour of hypochlorite-bleached cotton–nylon blends was inferior to that of bleached cotton; this effect was noticeable even with blends containing as little as 16% nylon.

The results of a trial carried out by Laporte Chemicals Ltd. indicated that the yellower appearance of the blend might be due to absorption of coloured impurities by the nylon during kier boiling. Also, that a combined scour and hydrogen peroxide bleach resulted in a much better white, comparable to a bleached all-cotton fabric. In order to obtain more information and to determine a method of bleaching cotton–nylon blends to give an acceptable white, the following trial was carried out.

Approximately 100 yd. of the cotton–nylon fabric used in the previous trial was divided into seven equal lengths and processed as follows—

together with sufficient caustic soda to give a pH value of 6·5.

The temperature was raised to 176°F. (80°C.) in 30 min. and maintained for a further 30 min., the cloth being then well rinsed and dried.

SAMPLE No. 3— The sodium chlorite bleach liquor was made up to the following formula (liquor : material 30 : 1)—

> 1·5 g. Sodium chlorite (80%)
> 1·0 g. Sodium pyrophosphate $\left.\right\}$ per litre
> 0·5 g. Lapol

The bath was adjusted to pH 4 and the temperature raised to 185°F. (85°C.), the previously wetted-out cloth being entered and run for 30 min. The cloth was then neutralised in a fresh bath with soda ash solution, and thoroughly rinsed and dried.

SAMPLES No. 4 AND 5— These two lengths were treated together in an approx. 1-vol. hydrogen peroxide combined scour and bleach liquor made

Sample	Bulk Treatment	Laboratory Treatment
1	Singed, desized, lime–soda ash boil, sodium hypochlorite bleach	Nil
2	Singed, desized, lime–soda ash boil, sodium hypochlorite bleach	Peracetic acid bleach
3	Singed, desized, lime–soda ash boil, sodium hypochlorite bleach	Acid sodium chlorite bleach
4	Singed and desized	Combined scour and hydrogen peroxide bleach
5	Singed, desized, and mercerised	Combined scour and hydrogen peroxide bleach
6	Singed, desized, lime–soda ash boil	Combined scour and hydrogen peroxide bleach
7	Singed, desized, mercerised, lime–soda ash boil	Combined scour and hydrogen peroxide bleach

The use of acid sodium chlorite solutions alone for bleaching the blended fabric was not investigated, but published information indicates their possible use for this purpose [e.g. 1, 8, 20]. The need for corrosion-resistant equipment, however, is retarding the development of this method for bleaching cellulosic fibres.

Details of Laboratory Treatments

Each sample was approx. 15 yd. long and the treatments were carried out on a winch machine.

SAMPLE No. 2— The cloth was wetted out and entered cold into a bath of the following composition (liquor : material 12 : 1)—

> 0·5 g. Sodium hexametaphosphate $\left.\right\}$
> 1·0 g. Lapol (Laporte) $\left.\right\}$ per litre
> 3·0 g. Peracetic acid (40%) $\left.\right\}$

up to the following formula (liquor : material 15 : 1)—

> 0·5 g. Caustic soda
> 1·75 g. Soda ash
> 7·0 g. Sodium silicate (78° Tw.) $\left.\right\}$ per litre
> 7·75 ml. Hydrogen peroxide
> 1·0 g. Lapol

The cloth was wetted out and entered into the cold liquor. The temperature was raised to the boil in 30 min. and maintained for 2 hr., the cloth then being well rinsed and dried.

SAMPLES No. 6 AND 7— The two lengths were treated together in a similar manner to Samples 4 and 5.

The concentration of hydrogen peroxide in the two bleaching baths for Samples 4–7 was determined at intervals; the results obtained are given in Table XVI.

TABLE XVI

Change of Concentration of Hydrogen Peroxide with Time during Bleaching

Strength of H_2O_2
Scour and Bleach Soln. (vol.)

	Samples 4 and 5	Samples 5 and 6
Start (cold)	1·07	1·05
After ½ hr., i.e. on raising to boil	0·87	0·82
After 1½ hr., i.e. after 1 hr. boiling	0·68	0·67
After 2½ hr., i.e. after 2 hr. boiling	0·57	0·58

The percentage whiteness reflectances of the various samples were measured on a laboratory reflectometer taking magnesium oxide as standard, i.e. 100%. In addition, a sample of the hypochlorite-bleached all-cotton fabric described in the previous section of this paper was similarly tested and included as a control. The results obtained are given in Table XVII.

TABLE XVII

Whiteness Reflectances (%)

Sample	Original Reflectance	Final Reflectance
Bleached all-cotton (control)	90·7	—
1	86·6	—
2	85·7	91·7
3	86·6	92·4
4	74·4	89·6
5	74·6	89·7
6	80·6	91·2
7	81·8	87·9

These results indicate that an acceptable white can be obtained by the combined scour and hydrogen peroxide bleach method or, alternatively, by aftertreating hypochlorite-bleached material with peracetic acid or acid sodium chlorite. There does not appear to be any advantage in kier-boiling the fabric before the scour–peroxide bleach, and premercerising has not contributed to an improvement in white detectable by the reflectometer. It should be noted that the aftertreatments were carried out on a winch machine, and that some modifications to the conditions of bleaching would be necessary in order to obtain comparable results on a dye-jigger.

The possibility that the soluble colouring matters originally present in the cotton are absorbed by the nylon during kier boiling has not been elucidated by this trial. Furthermore, it may be that this phenomenon would be more likely to occur during a caustic soda kier boil than during the lime–soda ash boil sequence—the matter requires clarification.

In order to determine if any "yellowing back" occurs under the influence of light, arrangements have been made to carry out exposure tests on representative cuttings of the bleached samples.

Tensile-strength and resistance-to-abrasion tests were carried out on the samples to give a comparative measure of the effect of the various bleaching processes. The results obtained are recorded in Table XVIII and indicate that the strength and wearing properties of the fabric have not been impaired by any of these processes. Previous test results on loom-state fabric (control) are given in Table XIV and Fig. 1.

CONCLUSIONS

All-nylon Material

(6,6, semi-dull)

SODIUM HYPOCHLORITE

(i) Has no bleaching effect.

(ii) Alkaline liquors (pH 10–11) do not cause degradation when applied under conditions conforming to good cotton-bleaching practice.

(iii) Weakly acid liquors (e.g. pH 6·6) cause severe degradation, even at 25°c.

HYDROGEN PEROXIDE

(i) Has a slight bleaching effect.

(ii) Alkaline liquors (pH 9·0) cause severe degradation when applied under conditions normally used for bleaching wool.

(iii) Alkaline liquors (pH 11·0) cause very marked degradation when applied under conditions normally used for bleaching cotton and cotton–viscose rayon mixtures.

TABLE XVIII

Tensile Strength and Abrasion Resistance of 80 : 20 Cotton–Nylon Blended Fabric bleached in various ways*

Sample	Tensile Strength (lb.)		Extension at Break (%)		Abrasion Resistance (rubs to hole)
	Warp	Weft	Warp	Weft	
1	170	117	14·5	19·8	6056
2	167	130	18·3	19·3	8193
3	180	132	19·8	20·9	4995
4	158	126	21·9	18·4	5849
5	164	117	17·9	17·0	6808
6	172	130	20·7	19·3	6264
7	167	121	17·2	19·5	5645

* Tensile strength, averages of 3 tests on Denison machine.

Abrasion resistance, averages of 4 tests on Martindale machine (samples 3, 4, 6, 7)

Abrasion resistance, averages of 3 tests on Martindale machine (samples 1, 2)

Abrasion resistance, averages of 2 tests on Martindale machine (sample 5).

(iv) Acid liquors (pH ca. 3·5–4·5) cause relatively slight degradation under ideal bleach-bath conditions.

PERACETIC ACID

(i) Has a bleaching effect.

(ii) Removes heat-setting discoloration and can be used when certain coloured effect threads are present.

(iii) The recommended bleaching method causes a drop in strength which, under normal conditions, should not be greater than about 10%.

SODIUM CHLORITE

(i) Has a bleaching effect.

(ii) Removes heat-setting discoloration but generally cannot be used in the presence of coloured effect threads because of its stripping action.

(iii) The recommended bleaching method causes little or no degradation.

Blends

WOOL–NYLON

HYDROGEN PEROXIDE— Blends containing up to 25% nylon can probably be bleached safely by the normal alkaline methods used for wool (requires bulk confirmation). For blends containing a large percentage of nylon, e.g. 50–60%, the acid methods are safer.

COTTON–NYLON

HYDROGEN PEROXIDE— Blends containing up to 25% nylon can probably be bleached safely by the normal alkaline methods used for cotton (requires bulk confirmation).

SODIUM HYPOCHLORITE— Normal cotton-processing conditions for white work do not cause tendering, but do not give an acceptable white.

Methods of Bleaching to give an Acceptable White

(i) Combined scour–hydrogen peroxide bleach.

(ii) Hypochlorite bleach, aftertreated with either peracetic acid or acid sodium chlorite.

N.B.— As mentioned in this paper, the use of acid sodium chlorite solutions alone for bleaching cotton–nylon blends has not been investigated, but published information indicates that it would be a satisfactory method.

* * *

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BRITISH NYLON SPINNERS LTD.

PONTYPOOL

MONMOUTHSHIRE

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Discussion

Mr. L. A. TELESZ: This paper is timely, because, apart from the classical work of Boulton and Jackson [2,3] on the effect of acids and light— some ten years ago— and more recently that by Davidson and Preston [21] on the effect of chlorine on nylon, relatively little has been published on the action of oxidising agents on nylon.

At the Hosiery and Allied Trades Research Association we, also, have done some work on the action of the oxidising agents referred to in this paper, and I am glad to say that our results are in general agreement with those of the present authors. An interesting observation we made was that, on peroxide treatment of increasing

severity, large strength losses were observed for a relatively small fall in viscosity. I do not know the true explanation, but obviously the mechanism of damage must be different from simple acid hydrolysis of the amide link.

Mr. SHAW: We thank Mr. Telesz for his comments on our paper and we are pleased to note that our results are in good general agreement with his own.

Mr. TELESZ: Why was relative viscosity chosen in preference to the fluidity test?

Mr. SHAW: There is no fundamental reason why the relative viscosity test was chosen in preference to the fluidity test— it is the standard method in use in B.N.S.

Mr. TELESZ: Have the present authors studied strength loss–viscosity relationships for oxidising agents over a range of conditions— and if so, with what results?

Mr. SHAW: We have not studied the strength loss–viscosity relationship for oxidising agents over a range of conditions. However, we appreciate the importance of such an investigation, and the matter has been drawn to the attention of our colleagues in the Research Department.

Mr. N. F. CROWDER: The normal alkaline method for bleaching wool with hydrogen peroxide is given as 16 hr. at 50°c. in 2-vol. solution. I would consider this to be excessive, as most wool bleachers would either bleach for 3–5 hr. at 50°c. or leave in a cooling bath overnight. Under these conditions, we find that hydrogen peroxide does not cause severe degradation even if the proportion of nylon in the nylon–wool mixture exceeds 25%. Would the speakers agree with this?

Mr. WILLSON: The methods chosen for bleaching trials were given to us as being widely representative of the processes used in the trade. In carrying out these trials we did not wish to err on the side of leniency, and preferred to record results for the most severe treatments. We are grateful to Mr. Crowder for his information, and would say that, whilst the time of 3–5 hr. might not cause degradation, it is clear that excessive time or an inadvertent rise in temperature could result in damage. From this point of view, the results quoted in the paper should be regarded in this case as indications of what could happen, and we hope that they will be a guide to the bleacher in establishing the process best suited to his plant and type of work.

Mr. H. R. HADFIELD: Cases have arisen of two nylon fabrics, dyed and pleated under the same conditions, behaving in different ways. In one case the result was satisfactory; in the other case very marked yellowing resulted. By which method should the material be prepared to avoid this trouble?

Mr. WILLSON: Woven and knitted nylon fabrics are prepared for pleating by the lightest possible setting treatment. Woven fabrics are jig-scoured and set in boiling water; whilst knitted fabrics are winch-scoured and dried on a stenter at well below setting temperature. If we can be sure that pleating conditions did not vary, e.g. in time of contact owing to change of pleat, or in temperature owing to lack of thermostatic control, the difference observed might possibly be due to variation in the oxidative condition of the original nylon yarn or polymer in the two fabrics— presumably manufactured at different times. We have not noticed this trouble as a direct comparison, but it is true that some fabrics tend to yellow more than others.

Some useful trials were carried out some time ago, in which simple reducing agents, e.g. sodium hypophosphite, were padded on to the fabric in order to "take the strain" of the pleating at high temperature. The results were quite promising but not outstanding, and could not be applied universally to coloured goods.

Mr. HADFIELD: Do I understand from Mr. Shaw's remarks that the nylon in a nylon–cotton mixture does not lose strength as a result of kier boiling?

Mr. WILLSON: Kier boiling has no degrading effect on nylon, either alone or in blends with cotton. The former condition would not, of course, arise, but a trial was carried out to note the effect of caustic soda under pressure at kiering strengths.

Mr. HADFIELD: Have the authors found that residual chlorine seriously reduces the light fastness of dyeings?

Mr. WILLSON: We have not carried out any work to see whether residual chlorine reduces light fastness on nylon. No complaints have been received on this score. The drop in tensile strength due to residual chlorine is more serious, and we experience trouble on that score rather than on account of loss of colour.

Dr. F. C. WOOD: How can a good white be obtained on soiled nylon underwear?

Mr. SHAW: Prevention is better than cure! It is advisable to wash nylon garments frequently in order to maintain a good white. A synthetic detergent should be used, thereby avoiding lime-soap deposits; the detergent should be used hand-hot, and gentle rubbing is often beneficial in obtaining the best results.

Occasions arise, however, when nylon garments become discoloured over a period of wear. This discoloration is usually referred to as "greying", and cannot be removed by bleaching with peracetic acid or sodium chorite. It is possible, however, to restore some of the original whiteness by a hot scour using a synthetic detergent containing perborate. This shock treatment should be used with reserve, because of possible damage to the fabric if applied repeatedly.

If slight yellowing occurs during the early stages of wear, this may be due to faulty finishing, i.e. heat-setting discoloration, which has not been subsequently bleached but merely covered with a fluorescent brightening agent. Such discoloration can be removed with peracetic acid or sodium chlorite, but not by the unfortunate housewife.

Mr. J. BOULTON: In considering the different relationships between loss of strength and fall in viscosity which result from the action of different bleaching agents, we should bear in mind the possibility that the chemical action of different oxidising agents on nylon may not be the same. Thus, in the case of hydrogen peroxide, per-acids, chlorites, and hypochlorites we are not necessarily always dealing merely with a polyamide of lowered molecular weight: we might have a chemically modified polymer. Do the authors know the extent to which chlorine is absorbed by nylon polymer in the case of the chlorine-containing bleaches? A study of the influence of chlorine absorption on the viscosity–strength relationship should clear up the problem.

Mr. WILLSON: The work described in this paper had an essentially practical purpose in trying to establish methods of bleaching nylon alone

or in blends, but some very interesting apparent anomalies soon occurred in the viscosity results. We are sorry that we did not have time to investigate these, since they could throw some light on the chemical behaviour of nylon. The problem has, however, been brought to the notice of our Research Department with a view to further work being carried out.

Mr. C. P. ATKINSON*: What procedure do the authors recommend for the removal of surface filaments from 100% nylon fabrics required in a sheer finish? An opinion on the relative merits of (a) gas singeing, (b) plate singeing, (c) cropping, etc. would be helpful, more particularly as it is obvious that to avoid "fused pilling" a good deal of experience is necessary.

Mr. WILLSON*: Though this question does not fall within the scope of the work described, it is nevertheless a very important one for the bleacher of spun nylon fabrics.

At the present time we can only say that singeing can be carried out on certain fabrics, notably those made from Schappe-spun yarns and possibly silk-spun yarns. Of course, the yarn itself plays a big part— whether single or folded, whether gassed or ungassed, and whether very hairy or fairly clean. The fibre ends are fused in the singeing process, and if this is excessive or if there are several long hairs on the yarn, a harsh, sandpapery handle will result. This is found on cotton-spun fabrics, where there are are obviously more loose fibre hairs per inch than on silk-spun fabrics.

Work is proceeding rapidly on this subject, and there seem to be indications that plate singeing is more effective in producing a clean soft fabric than is gas singeing. Cropping also is effective, but

is not easy to carry out on fine poplin constructions. It may be that, with very hairy fabrics, a cropping treatment before singeing will reduce the amount of beading and so improve the handle. All these treatments will reduce pilling in wear, which is not to be confused with the fused pilling referred to by Mr. Atkinson.

It is too early to answer the question more definitely than this, since information is still being gathered.

Mr. J. RAYMENT*: It has been suggested that the use with sodium chlorite of hydrolysable esters such as ethyl lactate gives efficient bleaching without the evolution of chlorine dioxide or metal attack. Bleaching efficiency is lower than that obtained from the same concentration of sodium chlorite used either with acid alone or by the buffered hydrogen peroxide technique. Can the authors state whether they consider that the method is suitable for use as a standing-bath technique, and if so, the rate of make-up required and whether they have been able to establish whether such liquors are corrosive to stainless steel?

Mr. SHAW*: We have not heard of this method, and we are not in a position to comment on its practical value. We suggest that the questioner takes the matter up with his supplier of sodium chlorite.

Mr. SHAW and Mr. WILLSON*: Since the paper was written, further results can be given. In the exposure tests referred to on p. 870 only the samples bleached with hydrogen peroxide did not "yellow back". The samples were exposed behind Vita-Glass for 10 weeks, commencing 1st March 1955— approx. 360 sun-hours.

* Communicated

The Achievement of High Wear-performance in Rayon Staple Fabrics with Crease-resist Finishes

H. W. BEST-GORDON and T. H. MORTON

Details are given of practical wear-assessment of crease-resist-finished rayon staple fabrics with the new Bocking Testing Machine (BFT Mark III). The machine determines resistance to flexing and to ball penetration; from these a duty factor is derived which correlates very well with resistance to premature wear.

Details are given also of the preferential resin pick-up of one fibre over another in blend fabrics, and the duty factors of an *ad hoc* series of satisfactorily produced gabardines.

The effects are described of some substances added to urea–formaldehyde resins for the purpose of producing various finishes on all-viscose rayon staple gabardines, and their effects on the duty factor are also discussed.

Finally, various conditions in the resin treatment of long-staple rayon fabric and their effects on wear-performance assessed by the duty factor are considered in detail.

1. INTRODUCTION

The application of a crease-resisting finish to a rayon staple fabric involves changes in a number of the textile, mechanical, and chemical properties of the fabric which are of importance to the ultimate consumer and to the finisher, the merchant, and the manufacturer. The more important properties which should be considered may be listed—

Group A Properties	Group B Properties
Handle	Strength
Drape	Extensibility
Crease-resistance	Tear-strength
Press-retention	Seam strength
Colour-fastness	Sewability
Fastness of finish to washing and dry-cleaning	Fastness of resin to washing
Wear properties	"Free formaldehyde" content
Absorbency and water-repellency	Storage odours
	Cutting-table properties

The Group A properties listed above are of direct interest to the ultimate consumer or wearer. The Group B properties listed are of interest mainly to the finisher, the manufacturer, and the merchant, although, for example, serious loss of tear and seam strength, or poor sewability, will result in an unsatisfactory garment in the hands of the ultimate consumer.

A point of interest concerning the above-listed properties is that, with one exception, all can be reliably assessed by well established laboratory or subjective tests: the exception is laboratory testing of wear properties. Here, until very recently, the position has been unsatisfactory, since all the accepted methods of testing for abrasion resistance were unreliable, for the laboratory results correlated rather poorly with actual experience in garment wear. A new method of forecasting wear by laboratory testing has been developed in the Bocking Laboratories, and details of this method will be given later.

Possible technical variations in the application of a crease-resisting finish can affect, to varying extents, the individual properties listed above; and it is improbable that a practical finish will achieve optimum performance in respect of every property. The finish applied will, therefore, be a compromise, and we believe that a better compromise will be achieved if the wear-properties — particularly in the heavy-end-use group of fabrics — are taken more into account.

It is the purpose of this paper to present some evidence which will be of use to the fabric designer and the finisher in the production of satisfactory heavy-duty rayon staple fabrics with crease-resisting finishes. We propose to discuss briefly the data available for blend fabrics and, in more detail, the type of finish and its necessary conditions of application for the production of a hard-wearing fabric. It would be desirable to include a consideration of influence of fabric structure, but this work is, as yet, incomplete. Our studies have, however, reached the point where it appears possible to state definitely that a well constructed fabric (in the commercial sense) may receive a finish representing a reasonable compromise in respect of all properties. We are certain also that some fabrics of low construction, where the desired properties can be obtained only by the application of, say, 20–25% of finish, have, generally, unsatisfactory wear-properties in heavy-duty end-uses.

2. DUTY FACTOR IN THE PREDICTION OF WEAR-LIFE

It is our experience that commercial complaints of poor wear properties in dress-weight materials applied to light end-uses are very small for rayon staple fabrics with crease-resisting finishes. This relative freedom from complaint in dress-weight fabrics is not due to the superiority of the finish applied to these fabrics, but rather to the fact that the wear-properties can be reduced considerably before an appreciable incidence of consumer complaints is likely to arise. In other words, the finisher can largely ignore wear-properties and make his compromise with particular reference to the other properties desired in the finished fabrics. This happy state of affairs does not continue when dress-weight fabrics are applied to typical heavy-duty end-uses, as in overalls.

Commercial records show that such a use of dress-weight fabrics is likely to lead to a much greater number of complaints.

In the post-war years, rayon fabrics with a crease-resisting finish have been constructed for a variety of heavy-duty end-uses. We define *heavy-duty end-use* as utilisation for— slacks, men's suits, uniforms, shirts, overalls, gym-slips, and rain-coats. Commercial records for such heavy-duty fabrics show that there has been, in the past few years, a considerable, if not a catastrophic, incidence of complaints of poor wear. We have examined a large number of heavy-duty garments, made from crease-resisted rayon staple fabrics, which have failed in field-trials and in the hands of ultimate consumers, and have noted that they fail almost always by reason of a particular kind of abrasive wear, notably at the turn-ups of trousers, cuffs, collars, raised seams, buttonholes, bottom hems, and pleat folds. The fabric tends to fail along a line or over a restricted area, where a raised part of the garment is subject to rubbing; there is little or no thinning of the fabric in contiguous areas. We propose the term *erosive wear* to denote such behaviour.

Erosive wear is quite distinct from flat abrasive wear, such as occurs at elbows, knees, backs, and seats of garments, where the fabric fails in wear by progression through threadbareness to thinness, finally failing by holing or tearing. Investigations in the Bocking Laboratories indicated that erosive wear was in no way correlated with the resistance to flat abrasion, as determined on most of the abrasion machines available and used in this country. It is, however, possible to obtain a very good correlation of erosive wear with a new measure of wear-resistance termed *duty factor*.

The duty factor is determined by means of an abrasion machine developed in the Bocking Laboratories— the BFT Mark III: a description of this machine and its application to crease-resist-finished rayon staple fabrics was given in a recent lecture by Breens and Morton[1]. The duty factor is obtained by combining the results of two different tests on the fabric, viz. the number of cycles required for a reciprocating weighted steel ball of $\frac{1}{8}$ in. diameter to penetrate the fabric, and the number of cycles of the machine required to break the fabric when flexed round a small but well defined cylindrical edge of 0·020 in. diameter.

The duty factor so obtained has correlated well with experience in field-trials and with consumer complaints. In a series of 60 fabrics quoted by Breens and Morton, there is no overlap in the group of duty factors corresponding to the satisfactory fabrics. The duty factor scale is long, ranging from less than 1, for unsatisfactory finishes on dress-weight and heavy-duty fabrics, to the order of 100 for carefully constructed blend fabrics with excellently applied finishes. Table I shows the range of duty factors to be expected in certain groups of rayon staple fabrics with crease-resist finishes.

TABLE I
Range of Values of Duty Factor

Fabric Type	Satisfactory Wear	Very Good Wear	Wear Properties probably better than required practically
Dress-weight fabrics in light-duty end-uses	1–4	4–7	7+
Heavy-duty end-uses	6–10	10–20	20+

3. APPLICATION OF CREASE-RESISTING FINISHES TO RAYON STAPLE BLENDS

Two points in the application of crease-resisting finishes to rayon staple blends are of importance. In the first place, the content of the resin should be adjusted for each blend in a way shortly to be described; in the second place, it should be noted that the use of certain blends may not only improve the aesthetics of the fabric, but also markedly affect the wear life as predicted by the duty factor.

In the application of crease-resisting finishes to blends of Fibro and Fibroceta (Courtaulds' rayon staple fibre, viscose and acetate respectively), it may be taken as a rough rule that five times as much resin will be taken up by the viscose rayon component as by the acetate rayon. Thus, if a blend containing 50% of viscose rayon staple and 50% of acetate rayon staple contains 6% of added resin, then the resin content of the viscose rayon is approx. 10% and that of the acetate rayon staple approx. 2%. In the finishing of such blend fabrics, therefore, in order not to overload the viscose rayon and so reduce its properties below a satisfactory level, the total amount of resin should be proportionately less than would be applied to a fabric of 100% viscose rayon. In the case of wool–viscose rayon staple blends, the same principle is valid as for viscose–acetate rayon blends. In the application of crease-resisting finishes to Fibro–Fibrolane blends, the Fibrolane (Courtaulds' regenerated protein staple fibre) as well as the Fibro will pick up resin, but since the properties of the Fibrolane can also be adversely affected by excess resin, it is desirable to apply an amount of resin distinctly less than that usual for 100% viscose rayon of the same weight and construction.

In the case of blends of viscose rayon with hydrophobic fibres such as nylon, Orlon, and Terylene, it should be assumed that the blending fibres will pick up none of the resin, and that the whole of the resin is taken up by the viscose rayon. Thus, in a blend containing 50% of viscose rayon and 50% of Orlon, an overall finish content of 5% represents a 10% pick-up of resin by the viscose rayon component.

In deciding the finish to be applied to a crease-resisted rayon staple blend fabric, the finisher should first decide the resin pick-up appropriate to the development of the desired properties in the viscose rayon component; this will usually be 8–15% of added resin, although smaller amounts may be required for worsted- or flax-spun materials

containing 4½-denier staple. The overall finish content of the blend fabric can then be computed, and the concentration of the dope set to achieve this result.

The duty factor has been determined for a large number of commercially produced rayon staple blend fabrics. Fabric structure has an obvious influence on the value of the duty factor, but sufficient ranges of blend fabrics have not yet become available for detailed guidance to be given on satisfactory structures.

The results of testing for duty factor an *ad hoc* series of satisfactory commercially produced and finished rayon staple gabardine fabrics of British, Canadian, United States, and South American manufacture are set out in Table II.

The conclusions to be drawn from Table II are—

(1) Satisfactory durable fabrics can be made from viscose and viscose–acetate rayon blends.

(2) The blending of certain fibres, particularly nylon, with rayon staple can increase the resistance

TABLE II

Duty Factor of Rayon Gabardines

Fabric	Fibre Composition	Weave	Resin Content (%)	Duty Factor
A	100% Viscose	Twill	—	10
B	100% Viscose (worsted-spun)	Twill	13	14
C	100% Viscose (cotton-spun)	Twill	10	18
D	75% Viscose–25% acetate	Twill	8	34
E	100% Viscose	Twill	8	17
F	80% Viscose–20% nylon	Twill	—	49, 71*
G	85% Viscose–15% nylon	Twill	—	19, 32*
H	85% Viscose–15% nylon	Twill	—	9
I	75% Viscose–25% acetate	Twill	—	13, 17*
J	100% Viscose	Satin†	11	5‡
K	70% Viscose–30% acetate	Satin†	7	8
L	85% Viscose–15% nylon	Satin†	15	35, 28, 54*
M	83% Viscose–17% Dacron	Satin†	12	24

* Individual figures are tests on pieces from separate finishing runs; the resin content noted refers to the first value.

† Fabrics J–M have a common construction: 5-end satin, 133 ends per inch, 1/20s cotton count, Z, twist-factor 3·75, 57 picks per inch, yarn as warp.

‡ The finish on fabric J is unsatisfactory, a low duty factor (instead of the level 10–15 which might be expected) resulting from a finish overbiased toward improvement of handle.

TABLE III

Effect of Additives on the Wear Properties of Rayon Gabardine

Nature of Additive	Additive	Composition of Dope (parts/100) Additive	BT 313	NH₄CNS soln.†	Polymer- isation*	Duty Factor	Ball (×10⁻³)	Plate (×10⁻³)
—	—	Nil	Nil	Nil	–	20+	78·3	41·0+
—	—	Nil	40	1	*	12·5	7·8	31·6+
Stiffener	Solvitose HDF (Scholten)	1	40	1	*	20+	22·1	20·0+
		1	Nil	Nil	–	20+	49·3	20·0+
	Gelatin	1	40	1	*	20	13·2	40·5+
		1	Nil	Nil	–	20+	61·7	20·0+
	Starch	1	40	1	*	15·6	9·5	43·3+
		1	Nil	Nil	–	20+	80·6	55·3+
	Dextrin	1	40	1	*	13·4	10·1	20·0+
		1	Nil	Nil	–	20+	60·5	48·0+
	Syton 2X (Monsanto)	5	40	1	*	3·9	17·4	2·2
		5	Nil	Nil	–	16·4	99·3	15·0
Softener (cationic)	Alcamine N (Allied Colloids)	0·5	40	1	*	15·8	13·2	20·0+
		0·5	Nil	Nil	–	20+	49·7	20·0+
Softener (non-ionic)	Lissapol N (ICI)	0·2	40	1	*	14·5	11·4	20·0+
		0·2	Nil	Nil	–	20+	78·9	20·0+
Softener (anionic)	Sapamine FL (CDC)	0·2	40	1	*	11·5	8·2	20·0+
		0·2	Nil	Nil	–	20+	62·3	20·0+
	Brilliant Avirol New Paste (Gardinol)	0·15 0·15	40 Nil	1 Nil	* –	8·9 20+	5·7 62·6	20·0+ 20·0+
Softener (water-repellent)	Velan PF (ICI)	6	40	1	*	14·6	11·5	20·0+
		6	Nil	Nil	*	20+	38·4	20·0+

† Catalyst addition, stated in terms of 20% solution.

* Fabrics marked * were polymerised and washed; the remaining fabrics were tested after drying and without polymerising.

to wear by a considerable factor. We believe that the more general use of nylon blends, containing, say, 85% of viscose rayon staple and 15% of nylon staple, is likely to provide the fabric designer with a means of achieving a tough and hard-wearing fabric which will give the finisher more scope and choice of finish, since with these fabrics it is not necessary to finish so near the optimum wear-properties as is the case with all-viscose or viscose-acetate rayon blend fabrics.

4. CONDITIONS WHICH AFFECT OPTIMUM RESULTS

It is obvious that when once a satisfactory system has been evolved whereby the performance of any crease-resisted fabric can be predicted, attention will be turned towards reviewing the conditions which will produce optimum results.

All who are directly associated with the practical application of resin finishes to textile fabrics are aware of the various difficulties encountered. These are due, in no small degree, to the fact that the full complexity of the process has never been generally understood.

There has been a tendency in the past to assume that the accepted methods for testing resin-content, in conjunction with certain other chemical and physical tests, are sufficient for control of the process and of fabric performance. In our opinion, this assumption is false, and we believe that plant control testing is widely different from performance assessment. Experience has shown that methods in general use for plant control are totally unsatisfactory diagnostically. The test results in such cases show nothing but the relationship of the present samples to those previously processed: in short, their function is to maintain a consistent product from delivery to delivery.

As stated earlier, the majority of crease-resist-finished rayon staple fabrics are satisfactory, but the residuum of unsatisfactory cloths has proved difficult to deal with. It has, in fact, been virtually impossible to identify the conditions which are directly responsible for fabrics of unsatisfactory wear-performance. The problem has been approached from many different points of view, with success restricted to very limited fields, and it has become obvious that the general feeling amongst merchants is to avoid the process entirely in heavier-duty fabrics. That such an approach is extremely bad for the finisher requires no further comment. Alternatively, many research investigators have attempted, with little success, to provide evidence on the more important factors in processing associated with improved wear-performance. In the past, studies have been made of resin content, directed at obtaining maximum crease-recovery. Other approaches have included the control of polymerisation by time, temperature, acidity, concentration, additives, etc. Some effective improvements have developed, but no entirely satisfactory formulae have been evolved for the commercial production of trouble-free fabrics.

The customary approach of chemical and physical tests has been seriously handicapped by two well recognised obstacles—

(1) The difficulty in the production of standard batch lots of urea–formaldehyde precondensate, with which the influence of resin concentration, catalyst, and time and temperature of polymerisation could be studied.

(2) Lack of a suitable method whereby the results obtained could be assessed in terms of consumer-service (especially in respect of wear-properties) with reasonable reliability.

We feel, however, that the use of duty factor assessment in conjunction with other tests can result in a much clearer understanding of the conditions required to produce a crease-resisting rayon staple fabric of good wearing properties. In our experiments, detailed below, we have, further, used only a commercially available urea–formaldehyde precondensate of constant and well defined properties.

5. INFLUENCE OF ADDITIVES TO UREA–FORMALDEHYDE RESIN ON THE WEAR PROPERTIES OF GABARDINES

Viscose rayon staple gabardine fabrics have given a considerable amount of trouble, since, in many cases, wear properties have been seriously impaired by resin finishes. The position has been aggravated considerably by the constant demand for firm finishes. Normally, crease-resist finishes confer a measure of firmness on any fabric, but the amounts of resin generally used to impart crease-resistant properties have fallen far short of producing the stiffness demanded by the trade. This has inevitably led to the use of excessively high resin concentrations or the inclusion of some product which acts solely as a stiffener. Many forms of stiffness are available, but starch or starch derivatives have been widely preferred. Alternatively, it has been recommended that small amounts of a more highly precondensed resin be used. These resins are commercially available as BT 6 (B.I.P. Chemicals Ltd.— BIPC), Calaroc UFB (ICI), etc.; they tend to polymerise between, rather than within, the fibres composing the fabrics.

Table I gave examples of approximate duty factor levels for light- and heavy-duty dress-wear fabrics; gabardines come into the heavy-duty end-use class. Experience has shown that, unless the stated levels are attained, consumer-experience will be far from satisfactory.

For the purpose of this paper, a good-quality gabardine (2/24s cotton-spun 15·7 Z/14 S, 3-denier 2½-in. matt Fibro, 76 ends, 154 picks, in 2/1 twill weave) was selected. It was felt that a decrease in wear-properties could be readily detected as a result of resin or a combination of resin–stiffener treatment. Consequently, a loom-state fabric was desized, scoured, and dried. Samples were then padded with the resin and/or additive stated to give 90–100% retention, and dried to uniform dimensions at 75°c. in a good air-circulating system. Polymerisation of the resin on the

resultant dry material was carried out for 3 min. at the standard temperature of 135°c. All the resin-treated samples were then washed in 0·25% soap and 0·25% sodium carbonate solution for 5 min. at 50°c., rinsed, hydroextracted, and dried to standard dimensions at 75–80°c. After drying, the samples were allowed to condition to standard regain.

The resin used was a commercially produced urea–formaldehyde precondensate, available to the trade as BT 313 (BIPC). The catalyst was ammonium thiocyanate.

The results of this series of experiments are given in Table III. The conclusions drawn are—

(1) All the fabrics in the series have a commercially acceptable level of wear-resistance.

(2) The effect of the resin treatment, in general, is to depress the ball value, making this the factor controlling the duty factor found. In the case of Syton 2X (Monsanto) additions, "negative lubrication" explains the abnormally low plate figure.

(3) There is little to choose between the use of starch, starch ether, or dextrin as a stiffening agent, as judged by the resulting duty factor.

(4) Anionic softeners appear to be a little less favourable than non-ionic or cationic softeners.

The effect on wear properties of adding highly precondensed resins such as BT 6 and Calaroc UFB to partly precondensed urea–formaldehyde has also been the subject of study. A section of the trade favours the use of this type in preference to the starch type of stiffening agent on the grounds that the finish is not so easily broken down and softened in wear. In this series of experiments, similar methods of resin application were used to those described earlier for the gabardine fabrics of Table III. The standard resin was BT 313 (BIPC) with ammonium thiocyanate used as catalyst (addition of 1% of a 20% solution). The results are shown in Table IV.

The plate figures demonstrate the lack of lubricity, particularly as the resin concentration is increased. This is largely due to the effect of resin deposited between the fibres, which results in a stiffening of the fabric, thus reducing the flexing properties. This effect is marked with increased quantities of Calaroc UFB.

It should be noted that the fabrics containing the higher proportions of stiffening agent would be rejected as unsatisfactory on the grounds of loss of tear strength.

Whilst the volume of resin used was maintained constant, it must be pointed out that Calaroc UFB contains 70% of solids, whilst BT 6 has 50%. This accounts, to some degree, for the higher resin figures with the former material. (Calaroc UFB, however, whilst reputed to be similar to BT 6, behaves differently in some ways, is of higher viscosity, and is a little less easy to bring into solution.)

6. INFLUENCE OF RESIN, CATALYST, AND TIME AND TEMPERATURE OF CURING ON THE WEAR PROPERTIES OF A LONG-STAPLE RAYON FABRIC

Probably one of the most outstanding examples of a fabric which has been satisfactory in the dress-goods field is Utility 1023 (4½-denier, 6-in. staple; flax-spun Fibro; 25s linen lea; 39 ends and 35 picks per inch in the grey)[2]. Millions of yards of this fabric have been produced in Northern Ireland, with outstanding success. However, when attention was turned to other markets and the fabric was used for overalls, experience was markedly changed, and there have been many serious complaints of poor wearability.

It has already been pointed out that end-use classification is essential. For light-weight dress wear, a minimum duty factor of 1–4 is desirable, whilst for heavier-duty wear this figure should be of the order of 6–10 (see Table I). Fabrics, therefore, which would be eminently satisfactory as dress material may be less satisfactory as overalls for use in shops and warehouses and may be totally unsuitable for the extreme conditions of heavy industries. No finisher can be expected to make full allowance for all the uses to which overalls may be subjected, but the maximum objective must be the more severe industrial conditions.

It is worth recording here that a number of crease-resisted U 1023 fabrics have been found to have a duty factor of less than 2 and are satisfactory as dress materials, but they would certainly break down in the mildest form of industrial use. In a particular example of complaint investigated.

TABLE IV

Influence of Mixed Resins*

BT 313	BT 6	Calaroc UFB	Added Resin (%)	Duty Factor	Ball (×10⁻²)	Plate (×10⁻⁹)
40	—	—	10·9	11·6	13·2	10·4
30	10	—	10·1	10·9	19·8	7·0
30	—	10	10·7	25·3	21·7	30·0
20	20	—	7·6	16·2	28·0	11·4
20	—	20	11·8	15·5	11·2	26·5
10	30	—	10·1	12·8	19·4	9·6
10	—	30	17·0	11·2	14·5	3·5
—	40	—	9·7	9·7	17·0	6·8
—	—	40	15·0	7·5	30·0	4·3

Preconrensed Resin (parts/100) spanning BT 313, BT 6, Calaroc UFB

* Catalyst in all cases 0·2 part/100. Fabrics polymerised for 3 min. at 135°c.

a duty factor of less than 1 was found; this material is known to fail in industrial use, but it is probable that it would not be highly satisfactory in dress-wear.

To avoid such failures, finishers in Northern Ireland and elsewhere have made changes in many directions, e.g. resin, catalyst, baking temperature, and baking time. Nevertheless, complaints have persisted, because the effect of any change could not be assessed in terms of erosive wear. It is of interest to see how the effect of various changes in application procedure can influence the wear properties of Utility 1023 fabric, as assessed by the BFT machine. The results, observations, and comments, however, apply only to the one specified fabric construction, and the following conclusions have been drawn from the experimental findings—

(1) Resistance to wear will fall rapidly as resin quantities are increased.

(2) Increasing amounts of catalyst reduce the wear properties without necessarily increasing the actual amount of resin added.

(3) The effect of prolonging heat treatments during resin curing is to reduce the wear properties.

(4) Curing temperatures are critical, and higher temperatures lead to decreased resistance to wear.

Excess of any one of the foregoing factors will reduce the wear performance of the fabric, and any attempt to effect improved finishes must take into consideration every factor.

It is appreciated that these factors, either singly or collectively, have been suspect for many years, but the relationship to wear properties has not been previously demonstrated.

Experimental

A standard procedure was adopted in resin application, a single factor only being varied in one series, the remainder being kept constant.

A suitable length of loom-state Utility 1023 fabric was desized, scoured, and dried. Samples were then padded (under conditions to be given in detail later) to give 90–100% retention of aqueous additive, and dried to uniform dimensions at 75°c. in a good air-circulatory system. Polymerisation of the resin on the resultant dry material was carried out as indicated in Tables V–VIII.

The samples were then washed in 0·25% soap plus 0·25% sodium carbonate solution for 5 min. at 50°c., rinsed, hydroextracted, and dried to standard dimensions at 75–80°c. After drying, the samples were allowed to condition to standard regain.

The resin used was the commercially available urea–formaldehyde precondensate BT 313; the catalyst was ammonium thiocyanate.

An asterisk (*) in Tables V–VIII indicates the more generally accepted commercial conditions. The quantities of resin and catalyst are based on 100 parts of the padding liquor, comprising concentrate with added water and catalyst solution. The catalyst is expressed as additions of a 20% solution of ammonium thiocyanate.

TABLE V
Influence of Added Resin
(Baked for 3 min. at 135°c.)

BT 313	NH_4CNS soln.	Added Resin (%)	Duty Factor
15	0·38	4·4	7·6
23	0·58	7·3	6·5
30	0·75	8·4	4·1
40*	1·00	11·8	3·3
50	1·25	15·4	2·4
65	1·63	18·5	1·7

TABLE VI
Influence of Catalyst Concentration
(Baked for 3 min. at 135°c.)

BT 313	NH_4CNS soln.	Added Resin (%)	Duty Factor
40	0	6·4	7·1
40	0·5	10·9	5·3
40	0·75	11·2	3·8
40*	1·0	12·2	2·4
40	1·25	12·2	2·1
40	1·5	10·3	1·9
40	2·0	10·8	1·5
40	3·0	10·9	2·4

TABLE VII
Influence of Time of Baking
(Baking temp. 135°c.)

BT 313	NH_4CNS soln.	Baking Time (min.)	Added Resin (%)	Duty Factor
40	1·0	0	2·8	7·2
40*	1·0	3	11·3	4·4
40	1·0	6	12·3	3·5
40	1·0	10	13·0	2·5
40	1·0	20	12·9	1·8
40	1·0	40	13·5	1·3

TABLE VIII
Influence of Baking Temperature
(Baking time 3 min.)

BT 313	NH_4CNS soln.	Baking Temp. (°c.)	Added Resin (%)	Duty Factor
40	1·0	—	1·8	6·4
40	1·0	100	7·1	5·6
40	1·0	120	9·7	3·9
40*	1·0	135	11·4	2·8
40	1·0	150	11·6	1·6
40	1·0	170	11·6	1·0

TABLE IX
Properties of Untreated Fabric without Added Resin

	Duty Factor	Ball ($\times 10^{-3}$)	Plate ($\times 10^{-3}$)
Scoured, fully relaxed ...	11·9	8·6	19·3
Set to dimensions ...	6	3·7	23·3
Heat-treated at 135°c. ...	5·7	4·2	8·9

The conclusions to be drawn from Tables V–IX inclusive are—

(1) Increase in any one of the factors— amount of added resin, amount of catalysts, baking time, and baking temperature— leads to a diminution in wear resistance.

(2) Utility 1023 is a fabric fully adequate for dress-wear, but is likely to be of marginal satisfaction for overalls used in severe conditions. A duty factor of 6 can be attained with special finishes, and this level should be adequate for fabrics intended for overalls intended for medium–heavy duty. The data quoted in Table IX for the fabric without resin finish suggest that a duty factor of 6, or at the most 10, is the highest level of performance which can be expected in U 1023 with an optimum crease-resisting finish. It is found generally, over a wide range of fabrics, that the duty factor of the finished fabric can at best approximate to the apparent duty factor of the original fabric, and with most commercial finishes it is distinctly less.

(3) The trend of results in Tables V–VIII is unequivocal: the levels of the asterisked standards are 3·3, 2·4, 4·4, and 2·8 respectively in the four series. A variation of this magnitude is usual in laboratory experiments on crease-resisting finishes — it is due to a combination of fabric and processing variables— and is probably paralleled by similar variation in duty factor in full-scale production.

7. DISCUSSION

The crease-resist process consists essentially in the preparation of a water-soluble precondensate of urea–formaldehyde, which is padded into a fabric in the presence of a catalyst or accelerator. The fabric is then dried on a stenter, and the resin polymerised or cured at high temperature to convert from a partly precondensed state into an insoluble form. The treated material is washed to remove the residue, and finally finished to dimensions by drying. It will be readily appreciated that the possible variations, both chemically and in the physical application, are very considerable. Factors which can vary are— molar ratio of formaldehyde to urea and the conditions of their interaction, degree of dilution of the precondensate as applied to the fabric, and type and concentration of catalyst. Drying may take place over a wide range of temperatures, and the final cure can be effected under a variety of time–temperature relationships. In addition, wetting agents, softeners, and stiffening agents can be added to the catalysed resin at the impregnation stage, and softeners to the final wash-off liquors. No less important is the fact that resinous products have to be applied to a complexity of fibre blends and fabric structures.

It is obvious that each individual finisher has established conditions of resin preparation and application which result in the production of fabrics with widely differing properties. That these differences exist has been indicated by one of us (H.W.B.-G.) in several publications, notably one in the Society's *Journal*[3] and a further, wider survey[4]; a third, more detailed study is in course

of preparation. It is not suggested, however, that all the variations have presented wear problems of the nature with which this paper is concerned, though this is largely because the majority of the materials have been used satisfactorily as dress or light-duty fabrics.

In the gabardine series, attempts have been made to show that additives, in the form of stiffeners, can be used without decreasing the wear properties of a fabric, providing care is taken in their selection. In fact, some actually give better wearability than does straight urea–formaldehyde. Their effect on toughness and lubricity is characteristic: when they are applied separately, the behaviour may be good, but added in conjunction with resin, they may cause unwelcome changes in ball or plate figure.

The use of softeners with resin shows how, in some cases, improved results are produced over the use of resin only, but in others a marked decrease in wear resistance is found.

These two types of additive— stiffeners and softeners— have opposed characteristics, but the addition of small amounts of softener to stiffened finishes for the purpose of lubrication is by no means unusual.

One serious adverse effect of stiffeners, particularly when used with resin, is to decrease tear strength, and this should be kept in mind in working out practical formulations.

When mixed resins are used, fabrics with poor tear strength can behave, seemingly, quite well as tested by the BFT machine. Any formulation of a stiff finish, therefore, should be checked for any adverse effect on tear and tensile strengths of the fabric.

The results shown in Table IV give some idea of the effect of mixed resins on duty factors. The extremely wide variation found is noteworthy; these results bear out, to some degree, the general experience of finishers. Presumably this is due, in no small measure, to the fact that surface deposits (as are produced by condensed resins) can fall anywhere on the surface, in the interstices of the fabric, or between the fibres themselves. The results of this rather irregular deposition are changes in fabric toughness and lubricity which, in our experience, are unpredictable.

In other work, the details of which are not recorded, it has been seen that factors such as resin solubility, time and conditions of precondensate storage, and ability of the fabric to pick up resin can adversely influence the final result. Whether or not these factors can be satisfactorily controlled, even after full investigation, is a matter for conjecture.

It is not suggested that it is customary to use these highly precondensed resins alone, but the results are included as evidence of their rather unpredictable behaviour. The use of gelatin in conjunction with urea–formaldehyde presents similar features; some finishers have included small quantities of methanol, with some measure

of success, to prevent insolubilisation of the gelatin in the resin bath.

In the Utility 1023 long-staple rayon series, the results reproduced in the tables demonstrate clearly how four important factors influence the wear resistance. The drop in performance with an increase of any one single factor indicates how difficult the process is to control, particularly when the end-use exceeds light-duty wear. It would appear that a duty factor of 6 could be attained using optimum conditions of less than 10% (possibly 6–8%) added resin, with the requisite catalyst quantity. The curing time must certainly not exceed 3 min., neither should the temperature of the fabric rise above 135°c.

It seems obvious that there must be a compromise on some aspect or other of fabric performance, and that the problem must be approached by deciding what is the maximum attainable standard consistent with wear performance. That the process requires careful control is evident, and no finisher can afford to exceed the maximum conditions if the fabrics are intended for heavy-duty wear. U 1023 fabrics, produced with less than maximum wear properties, are suitable for dresses, but if they are redirected into another, more searching end-use, complaints in varying degrees appear inevitable.

The recommendation to use less resin on flax-spun fabrics should not be surprising when it is recalled that finishing worsted-spun rayon fabrics with more than 7–8% of added resin usually results in a serious decrease in wearability. The similarity of these fabrics to U 1023 in fibre denier, staple length, and fabric type is significant. In addition, many worsted-spun types, designed essentially for the dress-goods trade, have found their way into use as gym-slips or kilts (i.e. heavy-duty end-uses) which have been the subject of commercial complaints because of breakdown occurring at the creased edges of either hem or pleat.

It has generally been assumed that sufficient resin should be applied to produce maximum crease-resistance; this we believe to be a dangerous maxim. By nature of fibre thickness and fabric construction, U 1023 has high crease-recovery properties, even without resin; furthermore, resin application frequently results in a decreased crease-

recovery performance [3]. It is reasonable, therefore, to point out that, on many occasions, the amount of resin applied has been in excess of that actually required for maximum crease-recovery, and an inevitable drop in wear performance has resulted.

The factors considered in the finishing of U 1023 have not taken into account any form of added lubricant or softener. Addition of such products will inevitably lead to improved wear performance, and this is evidenced in the untreated samples (Table IX), which have a high plate figure due to the lubricity of the structure.

A further approach towards improved performance would possibly lie in a modification of the constructional details of U 1023 fabric: from evidence presented in Table II, for example, it is probable that the use of a 15 : 85 nylon–Fibro blend would greatly increase the level of wear performance.

Whilst it would be presumptuous to attempt to lay down finishing conditions which will produce results to meet every requirement, we believe that we have demonstrated the possibility of an entirely new approach to the application of resin finishes capable of providing higher wear-performance in rayon staple fabrics.

*   *   *

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Discussion

Mr. D. A. DERRETT-SMITH: Could the authors comment further on the statement that erosive wear along a cuff is quite distinct from "flat abrasive" wear such as occurs at the elbows of a garment? I should have regarded the localised wear on the cuff as a degree of the same kind of wear as takes place at the elbow. Unsatisfactory wear resistance in both cases must be due to embrittlement by the resin.

Dr. MORTON: Evidence that flat abrasion-resistance and duty factor are virtually uncorrelated is given in the current issue of the

Society's *Journal*[1], and there it is further shown that duty factor alone correlates with "erosive wear", as at a cuff. We also know that, for the majority of commercial fabrics, a satisfactory duty factor is combined with a safe flat-abrasion value. In one case only have we met a wear-complaint on rayon staple suitings where flat abrasion at the knee was the cause of failure; here an abnormally poor flat value was combined with a reasonable duty factor.

It is certain, therefore, that flat abrasive wear and erosive wear are separate entities and should be tested separately. In practice, however, with a

fabric of known sound construction, the value of the duty factor is much more important than a determination of flat abrasive resistance.

Dr. N. LANDQVIST: Does any correlation exist between crease-recovery and duty factor of a given fabric?

Mr. H. W. BEST-GORDON: There is no strict correlation of crease-recovery of a given fabric with its duty factor. It is probable that, with increase of baking time, maximum crease-recovery is not achieved until the duty factor is falling off. Again, certain stiffening agents added to the dope mix can depress the crease-recovery without materially changing the duty factor.

Dr. F. C. WOOD: In reading the authors' most interesting paper I found myself most interested in Table III, in which various additives are shown to produce in the main no increase in duty factor and indeed in most cases a decrease. Apart from small amounts of softening agents such as the Sapamines, Lissapols, Velan, etc. for "handle purposes", none appears to be very beneficial, and some of us have long suspected that in a good many cases a finisher seems to delight in just putting in "plus a little something the other hasn't got" (with apologies to B.P.). May it not be that we are barking up the wrong tree? I should like the authors to comment on this implication I glean from their figures.

Dr. MORTON: To achieve the best wearing properties possible in a resin-finished spun rayon fabric, there is much to be said for keeping additives to a minimum. There is a demand for additional properties, such as increased stiffness, springiness of handle, and water-repellency, which make deviation from this concept necessary, but we appeal to all concerned to achieve a reasonable compromise in respect of all properties.

We are of the opinion that the degree of stiffness recently required commercially in rayon gabardines is unreasonable and has contributed notably to the development of poor wear properties.

Mr. C. P. ATKINSON: Could an opinion be expressed as to the relative effect on wear performance, as determined by the BFT Mark III testing machine, on, say, the same 100% rayon staple fabric, of polymerising in a baking stove where the heated air is simply circulated without any attempt to give a balanced air flow on both sides of the fabric by controlled impingement, as against using a machine which is adequately controlled in this respect?

Mr. BEST-GORDON: Since no comparative measurements have yet been made, we would hesitate to express an opinion on polymerisers designed with high and low air velocities. We would stress, however, that in the BFT Mark III machine there is available for the first time an instrument capable of deciding this point, as well as related points of detail in the whole commercial application of chemical finishes.

Mr. H. R. CRONE: The authors conclude from Table III that "there is little to choose between the use of starch, starch ether, or dextrin as a stiffening agent, as judged by the resulting duty factor". The results show that this is so, but it should be remembered that factors other than wear are involved in assessing the general suitability of a fabric for any end-use. Whether or not it would be desirable to use urea–formaldehyde crease-resist liquors without additives, the fact remains that there is a strong demand for urea–formaldehyde and allied finishes from which the "papery" handle has been removed and which at the same time retain high wash fastness. Of the three additives mentioned above only the starch ether Solvitose HDF, which has been designed for the purpose, will meet these requirements. While, therefore, starch and dextrin produced as satisfactory a duty factor as the starch ether, finishes with these as stiffeners would not be so acceptable.

Dr. MORTON: We are in full agreement with the remarks of Mr. Crone, and would again emphasise that every individual finish is a compromise which should be arrived at after full consideration of all relevant facts.

Mr. J. T. MARSH: However important and fascinating the study of morbid pathology may be, we should remember the millions of healthy people without whom the human race could not continue: those who are sick should consult a specialist. When the optimum conditions of treatment were established years ago, resistance to abrasion and actual wear trials were examined at some length in conjunction with other factors; the graphs shown by Mr. Best-Gordon exhibit such gross departures from those conditions in respect of time, temperature, and amount of catalyst that bad results are inevitable. With regard to the resin itself, the distribution is of at least equal importance to the amount. The ambiguous statement that "each individual finisher has established conditions of resin preparation and application which result in the production of fabrics with widely differing properties" cannot be accepted on either interpretation.

Dr. MORTON: We have already stressed in the introduction to our contribution that we are dealing with a minority of fabrics which break down rapidly in wear. We believe that we have established that there is a permissible latitude in processing conditions for women's dress-wear fabrics, but that the tolerance is less for fabrics intended for heavy-duty end-uses.

Our tests on fabrics produced in a considerable number of finishing works leads us to doubt fundamentally that Mr. Marsh's well established optimum conditions are used in practice. In fact, the variability of duty factor found on U 1009 fabrics can be due only to human fallibility, combined with systematic deviation from the "book". In this sense we justify our assertion of differing standards of work by individual finishers in this country and in North America.

Mr. BEST-GORDON: The allegedly ambiguous statement should be read in its full context. I have established the existence of wide variations between one finisher and another. At the same

time, I also appreciate, as stated earlier in this paper, that "millions of yards of this fabric have been produced in Northern Ireland with outstanding success".

Mr. G. ROBINSON: Do the authors consider that the methods of testing and assessment described could be applied in the case of pile fabrics? Several factors must be taken into account when considering the resistance to wear of a carpet. For example, in a closely woven Wilton, maintained in a clean condition, wear mainly takes place at the cut ends of the fibres on the surface; whereas in a low-grade carpet, which has not been kept very clean, grit penetrating to the base of the tufts abrades the sides of the yarns, causing fragments of fibres to split off. Do the authors consider that the action of dirt, particularly in the presence of moisture, is allowed for in the methods of assessment of wear described?

Dr. MORTON: We have some experience of the testing of carpets, but the methods differ considerably from those here discussed and may perhaps be left for later discussion. We agree, however, that the factors mentioned by Mr. Robinson are important for carpet wear.

Heavy soiling may have some effect on the wear life of suitings, for example, since the greasy dirt may act as a lubricant. This factor cannot, however, be significant, since a very good correlation exists between wear in the field and duty factor tests on the original clean fabrics.

Accelerated Hypochlorite Bleaching of Cotton

R. L. Derry

An attempt is made to determine the conditions under which warm or hot hypochlorite solutions can safely be used in cotton bleaching. It is shown that alkaline hypochlorite liquors, buffered at pH 10·5 or above, are very stable even on boiling. If the time of bleaching is reduced by a factor of 2·3 for each 10°c. rise in temperature, the quality of the bleach is maintained without appreciable increase in the extent of modification of the cellulose.

INTRODUCTION

Throughout the long history of bleaching by means of hypochlorite liquors of one kind or other there have been many attempts to accelerate the process. However, it is only since the widespread introduction of the fluidity measurement, as a means of detecting and estimating chemical damage caused to the cellulose, that it has been possible to discriminate between those processes in which saving of time is achieved at the expense of the textile qualities of the fibre and those in which no such high price is demanded for the advantages of an accelerated bleach.

In view of this, no useful purpose would be served by reviewing the many attempts that have been made with the object of utilising the attractive, but very dangerous, activity shown by neutral solutions of sodium or calcium hypochlorite. It is now nearly thirty years since Clibbens and Ridge[1] showed that the rate of oxidation of cotton cellulose by hypochlorite solutions is very dependent on pH and that, in the region of pH 7, when hypochlorous acid and the hypochlorite ion are present at approximately the same concentrations, the rate of attack on cellulose is greatly enhanced. The oxycelluloses formed under neutral and acid conditions are of the alkali-sensitive, reducing type, and any damage caused to the fibre may not be revealed until the yarn or fabric is subsequently treated with alkali[2]. Furthermore, the bleached material tends to become discoloured on storage, during a heat-treatment such as is applied during vulcanisation, or on processing under alkaline conditions, as, for instance, in printing with vat dyes, where the presence of reducing oxycellulose reveals itself not only by discoloration of the ground but also by bleeding of the prints during soaping.

Scholefield and Patel[3] showed that the photochemical oxidation of cellulose by hypochlorites may be greatly accelerated if the cellulose is dyed with certain yellow, orange, or red vat dyes of the anthraquinone type, while Derrett-Smith and Nodder[4] and Clibbens and Little[5] have confirmed this and shown that the magnitude of the effect is least with alkaline solutions (pH 11 and above) and greatest with neutral or acid bleach liquors (pH 7 or 4·5).

In view of this evidence there is little doubt that sodium hypochlorite is most advantageously applied to cotton textiles under alkaline conditions, preferably at or above pH 11. Under these conditions the bleaching process is more amenable to control, and any modified cellulose formed through overbleaching is non-reducing in character and therefore has little effect on the permanence of the white.

Another form of accelerated bleaching involves the addition of bromides or related compounds to hypochlorite liquors[6]. Claims are made in the relevant patents that a good white can be obtained in one stage and that the bleaching operation is less sensitive to alkalinity. The enhanced activity obtained in this way is due to the formation, in solution, of sodium hypobromite, which is a more powerful oxidant for cellulose than the hypochlorite from which it was formed, with the result that a high rate of bleaching is achieved, but only at the expense of fibre strength.

SCOPE OF THIS PAPER

It must be common knowledge to all bleachers that the rate of hypochlorite bleaching is increased by raising the temperature. In the work described in the present paper an attempt has been made to rationalise this process and in particular to determine the conditions under which warm or hot solutions of hypochlorite can safely be used in cotton bleaching. The work described is concerned, not with the mechanism of the reactions involved, but with the effect of temperature upon their rates.

The basic requirements for the success of any warm hypochlorite bleaching process may be stated as follows—

Firstly, the liquors themselves must be stable at any temperature likely to be employed. It would obviously be very difficult to control a process in which the available oxygen content of the feed liquor depended upon the age of the solution.

Secondly, the rate of oxidation of the impurities in the fibre must be related in a simple manner to temperature, so that some form of reproducible control is possible.

Thirdly, since sodium hypochlorite is not an ideal bleaching agent and therefore, even under the best conditions of application, some slight attack on the cellulose is to be expected, it is essential that the effect of temperature on the rate of attack should not be significantly greater (from a practical viewpoint) than the effect upon the rate of bleaching.

The last requirement, but not least in importance, is that the quality of the bleach must not be impaired by the use of temperatures higher than those normally encountered in bleachcrofts.

These four basic requirements will be dealt with in turn.

STABILITY OF BUFFERED SOLUTIONS OF SODIUM HYPOCHLORITE

For the sake of convenience and because under certain circumstances bleaching with hypochlorite might possibly be carried out in a steamer, the stabilities of boiling solutions of sodium hypochlorite were determined.

Experimental Procedure and Results

A series of bleach liquors was prepared by dilution of commercial sodium hypochlorite. The liquors were all 0·04 N. in available oxygen and were buffered at constant alkali-metal-ion concentrations over the pH range 7·7–13·0. They were boiled under reflux over a free flame in resistance-glass apparatus, and a slow stream of nitrogen was passed through the liquor to remove gaseous products of decomposition. Corrections were applied for the small changes in concentration caused by loss of moisture (0·7% per hour) through the condenser. Specimens of liquor taken at intervals throughout a 3-hr. experiment were analysed iodometrically for available oxygen.

The stability of hypochlorite liquors at the boil was found to increase with increase in pH (Table I).

TABLE I

Initial pH	Buffer System	Loss (%) of Available Oxygen after (min.)—			
		30	60	120	180
7·7	Na$_2$B$_4$O$_7$–HCl	21·4	33·9	51·5	60·4
8·6	Na$_2$B$_4$O$_7$–HCl	5·9	7·9	14·6	20·7
9·2	Na$_2$B$_4$O$_7$	3·4	4·7	10·0	15·5
10·4	KH$_2$PO$_4$–NaOH	2·4	2·9	5·6	7·6
11·1	Na$_2$CO$_3$	1·4	3·1	5·1	5·1
12·0	NaOH	1·5	3·4	4·8	6·0
13·0	NaOH	1·5	2·9	4·6	5·6

Above pH 11 only 5–6% of the hypochlorite was decomposed when the solution was boiled for 3 hr. A smooth curve relates the loss of available oxygen to the initial pH of the solution (Fig. 1).

Hypochlorous acid is a weak acid and its salts are largely hydrolysed in solution. Davidson [7] has determined the apparent dissociation constant in dilute solution and has found a value of $3·7 \times 10^{-8}$ at room temperature. Thus at pH 7·43 50% of the acid is in the free (unionised) state, while at pH 8·7 the proportion has fallen to 5%; and by calculation
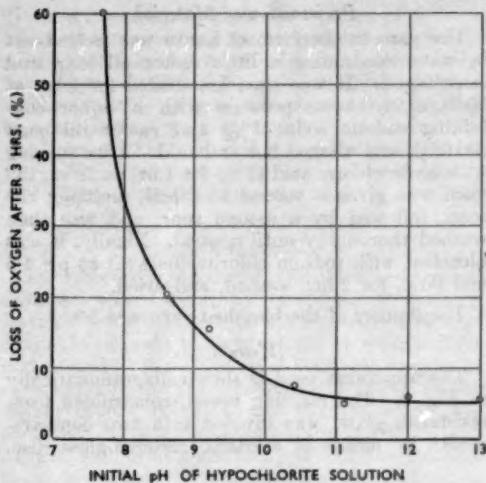
FIG. 1

it can be shown that above pH 10 the hypochlorite present in a bleach liquor is almost entirely present as the hypochlorite ion. This situation is reflected in the stability of the liquors at the boil, although the position is complicated by the presence of the buffer salts.

At pH 8·6 the rate of decomposition is sufficiently high to permit accurate estimations of the fate of the available oxygen to be made. Of the hypochlorite decomposed in 8 hr. at the boil (34%) only 2·6% of the available oxygen appeared in the form of chlorate, while the rest was lost from the system; there was no significant change in the total chlorine content of the liquor. There is no evidence that the slow reaction by which hypochlorite ion and hypochlorous acid interact to yield chlorate is appreciably accelerated by rise in temperature.

These results show clearly that alkaline hypochlorite liquors, at or above pH 10·5, are exceptionally stable, and that wastage should be negligible at any temperature it may be practicable to use for bleaching.

EFFECT OF TEMPERATURE UPON RATE OF OXIDATION OF CELLULOSE

For present purposes the bleaching of cellulosic material may be regarded simply as two oxidation processes taking place simultaneously. One of these, the bleaching reaction proper, involves oxidation of non-cellulosic materials in the fibre and proceeds at a much higher rate than the other, which is a heterogeneous reaction between the hypochlorite liquor and the cellulose of the fibre. In order to determine the effect of temperature on this second reaction, a series of "bleaching" treatments was applied at temperatures ranging from 20°C. to 80°C. to thoroughly scoured and bleached 20s cotton yarn.

Preparation of Material

The yarn in the form of hanks was wetted-out in water containing a little castor oil soap and centrifuged. It was then kier-boiled for 3 hr. at 30 lb./sq.in. excess pressure with a liquor containing caustic soda (1%) and castor oil soap (0·15%), and washed hot and cold. After souring with hydrochloric acid (1%) for 1 hr. at 20°C., the yarn was given a second kier boil, omitting the soap, followed by a second sour, and was then washed thoroughly until neutral. Finally, it was bleached with sodium chlorite (0·04 N.) at pH 4·5 and 90°C. for 2 hr., washed, and dried.

The fluidity of the bleached yarn was 3·9.

Method

The apparatus used is shown diagrammatically in Fig. 2. The reaction vessel, constructed from resistance glass, was divided into two compartments by means of a coarse sintered-glass disc.
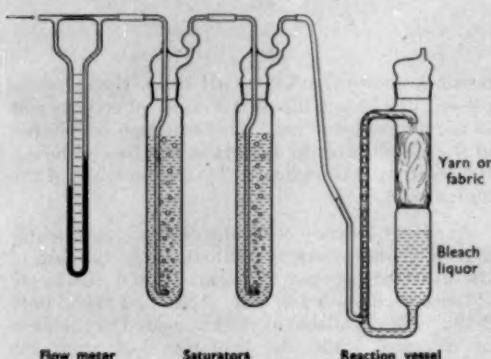
FIG. 2

Cotton yarn (20 g. dry weight) was placed in the form of a hank in the upper compartment, and 250 ml. of bleach liquor was introduced through the side-arm into the lower compartment; 150 ml. more (giving a liquor : cotton ratio of 20 : 1) was poured on to the yarn at the beginning of the experiment. Circulation on the "air-lift" principle was obtained by means of a stream of nitrogen, which was passed through saturators immersed alongside the reaction vessel in the thermostat. In this way evaporation was minimised. The apparatus containing the cotton and the bleach liquor were brought to the required temperature before circulation was started. Liquor specimens were taken at intervals and analysed for available oxygen, and corrections were applied for the small changes in concentration caused by the removal of specimens.

Results

In a preliminary trial the cotton cellulose was treated with bleach liquors buffered at pH 11 with sodium carbonate, ranging in concentration of available oxygen from 0·0064 N. to 0·94 N. The treatment was continued for 16 hr. at 20°C. or
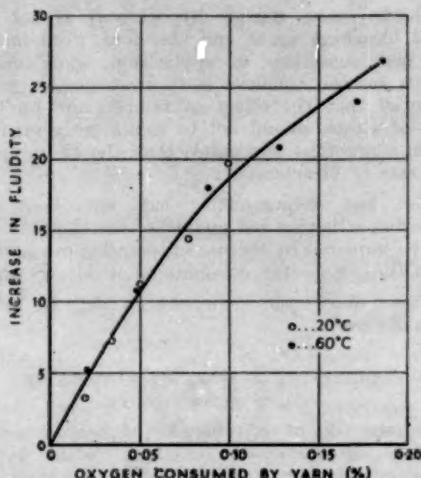
FIG. 3

30 min. at 60°C., and the results (Table II) serve to show that the relation between the amount of oxygen consumed and the rise in fluidity is the same at both temperatures (Fig. 3). Chemical attack on the cotton at pH 11 is therefore a function of oxygen consumption and, within the limits of the experiment, is independent of the temperature, and therefore of the rate, of the reaction. The oxycellulose formed at 60°C. closely resembles that produced at 20°C., for the changes in copper number and carboxyl group content are nearly the same for equal consumptions of oxygen (Fig. 4).
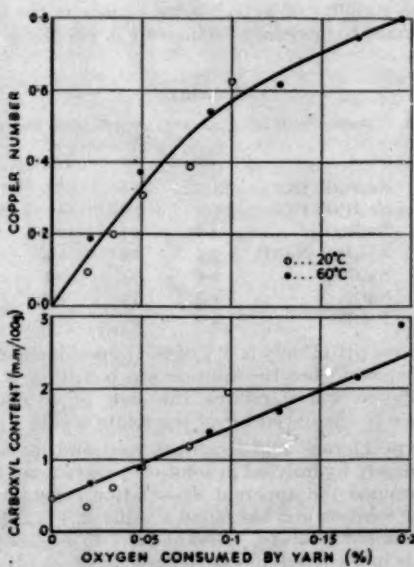
FIG. 4

TABLE II

Oxygen in Soln. (% on wt. of cotton)	After 16 hr. at 20°c. Oxygen consumed (%)	Increase in Fluidity	After 30 min. at 60°c. Oxygen consumed (%)	Increase in Fluidity
0·103	0·020	3·3	0·021	5·3
0·301	0·034	7·3	0·049	11·0
0·608	0·050	11·2	0·088	18·1
0·911	0·077	14·4	0·127	20·9
1·51	0·099	19·7	0·195	26·9

DETERMINATION OF TEMPERATURE COEFFICIENT

When purified cotton cellulose is treated with sodium hypochlorite at pH 11, the time taken for a given fraction of the reaction to be completed is independent of the initial concentration of available oxygen, and the reaction is therefore of the first order. The kinetic equation for a reaction of the first order—

$$k = \frac{1}{t} \ln \frac{a}{a-x}$$

where a = initial concentration of available oxygen and x = concentration after time t, may be applied to the present results; it gives a very nearly constant value for k, the velocity constant, at any given temperature. From the values of k for a range of temperatures the temperature coefficient of the reaction may be calculated. Alternatively, the reciprocal of the time in which a given fraction of the available oxygen is consumed may be used as a measure of reaction rate. The advantage of the latter method is that it is equally applicable to the more complex reactions involved in bleaching that do not obey the first-order law.

Experimental

The thoroughly scoured and bleached cotton cellulose was treated at temperatures ranging from 20° to 80°c. with a bleach liquor (0·0375 N. in available oxygen) buffered at pH 11 with sodium carbonate (0·1 N.). The total available oxygen in each experiment was equivalent to 0·6% on the weight of dry cellulose, and the treatment was continued until at least one-sixth (0·1%) of the oxygen had been consumed. From the relation between oxygen consumption and time of treatment (Table III) the time $t_\frac{1}{6}$ required for a consumption of 0·1% of oxygen at each temperature was derived. This varied from 47·7 hr. at 20°c. to

TABLE III
Effect of Temperature on the Hypochlorite Oxidation of Cotton Cellulose

Time, t	Oxygen Consumption (% on dry wt. of cellulose) after time t at—						
	20°c.	30°c.	40°c.	50°c.	60°c.	70°c.	80°c.
(min.)							
5	—	—	—	—	0·020	0·041	0·064
10	—	—	—	—	0·037	0·067	0·119
15	—	—	0·012	0·022	0·044	0·095	0·181
20	—	—	—	—	—	0·117	—
30	—	0·013	0·017	0·037	0·076	0·166	—
45	—	—	—	—	0·109	0·210	—
60	0·002	0·018	0·032	0·063	0·140	—	—
(hr.)							
1½	—	—	—	0·078	0·184	—	—
2	—	0·030	0·050	0·109	0·217	—	—
2½	—	—	—	0·123	—	—	—
3	—	—	0·065	0·141	—	—	—
4	0·013	0·045	0·081	0·182	—	—	—
5	—	—	0·103	0·202	—	—	—
6	—	—	0·117	—	—	—	—
7	0·018	0·069	0·131	—	—	—	—
24	0·051	0·146	—	—	—	—	—
31	0·071	0·172	—	—	—	—	—
48	0·102	—	—	—	—	—	—
55	0·114	—	—	—	—	—	—
74	0·147	—	—	—	—	—	—

TABLE IV
Temperature Coefficient of Hypochlorite Oxidation of Cotton Cellulose

Temperature, °c. ...	20	30	40	50	60	70	80
Time, $t_\frac{1}{6}$ hr.	47·7	12·5	4·80	1·88	0·67	0·254	0·136
Rate of oxidation relative to that at 20°c. ...	1·0	3·8	9·9	25·4	71·2	188	355
Temp. coefficient* ...		3·80	2·57	2·63	2·75	2·69	1·86
				Mean value = 2·66			
k, sec.$^{-1} \times 10^8$ ...	1·02	4·78	9·16	23·6	56·2	168	394
Temp. coefficient* ...		4·68	1·92	2·58	2·38	2·99	2·34
				Mean value = 2·82			

* For 10°c. increase in temperature

<div align="center">TABLE V</div>

Temperature, °c. ...	20	30	40	50	60	70	80
Duration of treatment, hr.	74	31	7	5	2	0·75	0·25
Oxygen consumed, % ...	0·147	0·172	0·161	0·202	0·217	0·210	0·181
Rise in fluidity	22·2	23·3	23·5	25·9	27·3	25·9	25·2
Oxygen consumed per unit rise in fluidity, mg.	6·6	7·4	6·9	7·8	7·9	8·1	7·2

<div align="center">Mean = 7·4 ± 0·4</div>

approx. 8 min. at 80°c. Mean values of the velocity constant k were obtained from all the individual estimations of oxygen consumption and not from a single intercept on the curves. From the slope of the straight line relating log $(1000/t_4)$ or log k to temperature, the temperature coefficient of the reaction was found to be approx. 2·7. The results are summarised in Table IV. The single-intercept method gives the more consistent results, particularly when t_4 is neither exceptionally large nor exceptionally small.

At the end of each treatment the yarn was removed, treated with a solution of sodium sulphite (1%), washed, and dried. The relation between oxygen consumption and rise in fluidity was found to be independent of the rate of reaction. On the average, a rise in fluidity of one unit was caused by the consumption of 7·4 mg. of oxygen per 100 g. of dry cellulose (Table V).

It is concluded from this section of the work, and confirmed later, that if the time of treatment of scoured cotton with a hypochlorite liquor of given composition is reduced by a factor of 2·7 for each 10°c. rise in temperature the consumption of oxygen and the extent of chemical modification of the cellulose will be very nearly constant.

OXYGEN CONSUMPTION OF MILDLY SCOURED COTTON DURING HYPOCHLORITE BLEACHING

The bleaching reaction proper occurs between the impurities in the cotton and the hypochlorite. Consequently the consumption of oxygen and its relation to rise in fluidity must change considerably with the thoroughness of the scour. However, as with purified cotton cellulose, the relation between oxygen consumption and rise in fluidity was found to be independent of the rate of bleaching. This is illustrated by results shown in Fig. 5, which refer to bleaching trials conducted on mildly and thoroughly scoured 20s cotton yarn in the laboratory apparatus already described and on a desized poplin (144 × 76, 50s × 50s) on a wince machine. The temperatures used ranged from 20°c. to 60°c. The consumption of 0·55% of oxygen by the poplin, of 0·29% by the mildly scoured yarn, and of 0·025% by thoroughly scoured yarn was accompanied by the same rise in fluidity of 5 units, which is about the maximum acceptable in a well conducted technical bleach.

Assessment of the quality of a bleached cloth remains very much a matter for individual judgment. Reflectometers are, however, useful in comparing the brightness of a particular cloth which has been bleached in different ways. As measured by the E.E.L. instrument, brightness

increases nearly linearly with consumption of oxygen until maximum brightness is almost reached. Up to this point the rise in fluidity exceeds 5 units. Then there is a sharp inflection
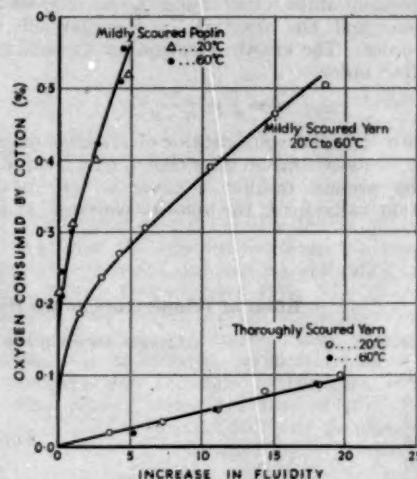
<div align="center">FIG. 5</div>

in the curve, and further improvement in brightness is secured only at the expense of severe chemical tendering. The general shape of the curve and the point of inflection are not altered appreciably by the rate of bleaching, at least over the range considered.

EFFECT OF TEMPERATURE UPON RATE OF BLEACHING

In order to accentuate differences between bleaching treatments, cotton yarn (20s count) that had received only a mild scour lasting 1 hr. at 90°c. in a liquor containing soap (0·2%) and sodium carbonate (0·5%) was used in the following experiments. They were conducted at temperatures from 10°c. to 60°c. with a liquor ratio of 20 : 1; as before, hypochlorite liquors (0·0375 N. in available oxygen) buffered at pH 11 were employed.

Because of the greater consumption, the time required for half the available oxygen to be used up (0·3% on the cotton and equivalent to a rise in fluidity of 5–6 units) was determined from the curves and used to estimate the rate of bleaching at each temperature (Table VI).

TABLE VI

Effect of Temperature on Rate of Hypochlorite Bleaching

Temperature, °c.				10	20	30	40	50	60
Time, $t_{\frac{1}{2}}$* min.	...	...	...	832	388	162	66	29	14
Rate of bleaching relative to that at 20°c.				0·47	1·0	2·40	5·88	13·4	27·7
Log (1000/$t_{\frac{1}{2}}$)...	...	...	...	0·08	0·42	0·79	1·18	1·54	1·85
Temp. coefficient	...	...	...		2·19	2·34	2·45	2·29	2·04

Mean value = 2·26

*$t_{\frac{1}{2}}$ = Time required for the consumption of half the available oxygen

The relation between the logarithm of the rate of consumption of oxygen and temperature is linear (Fig. 6), and the slope may be used to measure the temperature coefficient. The mean value obtained
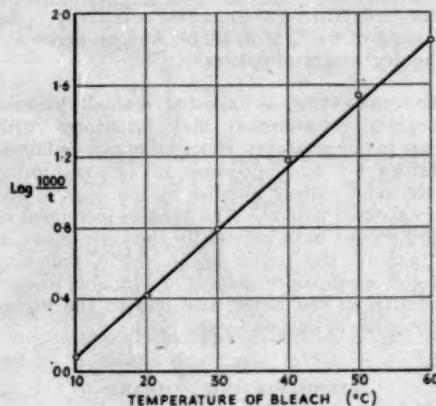

FIG. 6

in this way, 2·26, is lower than that for the oxidation of pure cellulose (2·70), but, because the bleaching reactions proceed at a much higher rate, this difference is not of any technical importance, as will be seen later.

THE STRENGTH–FLUIDITY RELATIONSHIP OF COTTON BLEACHED AT 20°C. AND 60°C.

For a given material the quality of the bleach and the rise in fluidity sustained in the process are determined by the consumption of oxygen. So far in this work complete reliance has been placed on the fluidity measurement as an index of chemical damage, irrespective of the conditions under which it was caused. This is completely justifiable whenever the tendering is uniform in character, but since it is possible that at high rates of bleaching the surface of the yarn might be more severely attacked than the interior, it was considered essential to establish that the strength–fluidity relation of yarn bleached with hot solutions of hypochlorite is not significantly different from that of yarn processed in the conventional manner.

Experimental

The bleaching trials were made on 40s ring-spun Egyptian cotton yarn having a twist factor of 3·2. Separate hanks of yarn were given either a light scour with soap and sodium carbonate or two successive kier boils with caustic soda as described (but, of course, omitting the bleach with sodium chlorite) and were then wound on cones. The method of sampling the yarn for tensile strength tests was that described by Midgley and Peirce [5] as the "cut skein" method, in which alternate threads serve as controls, and the effect of spinning irregularities is minimised. Parts of the cut skein were bleached with 0·04 N. sodium hypochlorite at pH 11 in an "infinite" bath for a standard time T_{20} of 3 hr. at 20°c. and for multiples of this time in geometric series (2, 4, 8 × T_{20}). In addition, bleaching treatments were applied at 60°c. for equivalent periods. These were calculated using the temperature coefficient of 2·28, and ranged from 6 min. 40 sec. (T_{60}) to 53 min. 17 sec. (8T_{60}). One-hundred tensile strength measurements were made per specimen, and fluidities were determined on the broken threads. Table VII gives the results, from which it is concluded that the strength–fluidity relationship is not significantly affected by the high rate of bleaching at 60°c., although it is noteworthy that under otherwise the same conditions of treatment the mildly scoured yarn has suffered more chemical attack of the cellulose than the thoroughly scoured yarn. Only when

TABLE VII

Strength–Fluidity Relations of 40s Yarn bleached at 20°C. and at 60°C.

Duration of Treatment	Mildly Scoured		Thoroughly Scoured	
	Loss of Tensile Strength (%)	Fluidity Rise	Loss of Tensile Strength (%)	Fluidity Rise
(hr.)	TEMPERATURE = 20°C.			
T_{20} = 3	7·8	6·7	5·2	3·5
2T_{20} = 6	8·9	7·4	5·6	6·5
4T_{20} = 12	12·0	10·7	12·8	9·9
8T_{20} = 24	23·3	16·4	19·6	14·4
(min.)	TEMPERATURE = 60°C.			
T_{60} = 6·66	5·8	5·6	5·0	3·0
2T_{60} = 12·3	8·9	9·2	10·2	8·0
4T_{60} = 26·6	18·5	15·8	18·5	11·7
8T_{60} = 53·3	29·7	22·7	31·5	20·6
Mean initial breaking load ...	258 g.		252 g.	
Mean initial fluidity ...	2·1		3·6	

TABLE IX

Temp. (°c.)	Duration of Bleach (min.)	Oxygen Consumption (%)		Copper Number		Carboxyl Content *(millimoles/100 g.)		Increase in Fluidity		Reflectance Factor of Fabric
		Yarn	Fabric	Yarn	Fabric	Yarn	Fabric	Yarn	Fabric	
Unbleached controls ...	0	0	0	0·18	0·37	2·55	4·33	1·9*	2·7*	0·60
20	360	0·29	0·41	0·24	0·25	1·85	2·65	3·9	2·7	0·89
30	133	0·29	0·41	0·25	0·27	1·86	2·71	4·6	2·8	0·88
40	49·4	0·30	0·40	0·30	0·26	1·88	2·64	5·5	3·2	0·89
50	18·3	0·27	0·39	0·27	0·27	1·85	2·56	5·3	3·3	0·88
60	6·8	0·26	0·34	0·28	0·29	1·87	2·55	3·9	2·7	0·87

*Fluidity

the yarn has been considerably overbleached is the effect of the higher temperature coefficient of the reaction involving oxidation of cellulose (2·7) apparent.

From the curves relating loss of tensile strength to rise in fluidity it is concluded that at the two temperatures a given rise in fluidity has the same significance within the limits of the experiment (Table VIII).

TABLE VIII

Rise in Fluidity	Loss in Tensile Strength (%) sustained by—			
	Mildly Scoured Yarn bleached at—		Thoroughly Scoured Yarn bleached at—	
	20°c.	60°c.	20°c.	60°c.
5	4·5	4·2	4·5	6·1
10	12·5	11·0	12·5	14·1
15	20·8	18·5	20·8	22·5

Specimens bleached for equivalent periods at the two temperatures were found to be equally well bleached, but, as anticipated, the quality of the bleach obtained on the thoroughly prepared ground was superior to that obtained on the mildly scoured yarn.

REPRODUCIBILITY OF RESULTS

Most of the experiments described in this paper have been concerned with general relationships. In technical practice, of course, a specific result, namely a good-quality white with only a small rise in fluidity, is demanded, and this result must be capable of being reproduced consistently. That this is possible, given control of the initial concentration of available oxygen and the time and the temperature of the bleach, is shown by the results recorded in Table IX. The bleaches were carried out on mildly scoured yarn or poplin fabric and, in addition to the standard tests of fluidity, copper number, and carboxyl-group content, measurements of brightness were made by means of an E.E.L. reflectometer on the fabric specimens with magnesium carbonate as the standard white surface (reflectance factor 1·00).

In the bleaching of mildly scoured cotton a temperature coefficient of 2·3 would normally be used to calculate equivalent periods of bleaching at different temperatures. However, in this experiment the opportunity was taken to determine what effect the adoption of the higher value, found to be operative in the oxidation of cellulose (2·7), would have on oxygen consumption and the quality of the resulting bleach. The bleach liquors (0·0375 N.) contained initially the equivalent of 0·6% of available oxygen expressed on the dry weight of cotton.

The results show, as expected, a small decrease in oxygen consumption and brightness with increase in temperature. Removal of non-cellulosic impurities led to a decrease in carboxyl-group content (and copper number in the case of the lightly scoured poplin). The average increment of fluidity proved to be greater for the yarn (mean = 4·6) than for the poplin (mean = 2·9), reflecting the lower mean concentration of available oxygen in solution in the latter case due to the higher consumption of oxygen by the cloth.

DISCUSSION AND SUMMARY

The rate of consumption of oxygen— and therefore the rate of bleaching— with hypochlorite liquors buffered at pH 11 increases by a factor of 2·3 for each 10°c. rise in temperature. When, therefore, the time taken to bleach yarn or cloth at one temperature is known, the corresponding time at a lower or a higher temperature, under otherwise the same conditions, may readily be calculated.

The amount of oxidisable material left in the yarn or fabric from the preceding preparatory processes varies very considerably, depending particularly on the severity of the scour, which may range from a simple wetting-out treatment to a double kier-boil carried out with caustic liquors under pressure. The oxygen consumption required for a satisfactory bleach must therefore be found by experiment, and sufficient allowance made for possible variations within and between batches of material.

It is unnecessary, perhaps, to add a warning that the temperature and the duration of the bleaching treatment must be controlled with care. This may be illustrated by the series of curves depicted in Fig. 7, which relate the amount of oxygen consumed by a mildly scoured cotton yarn to the temperature and the duration of the treatment.

ΔF = Increase in fluidity
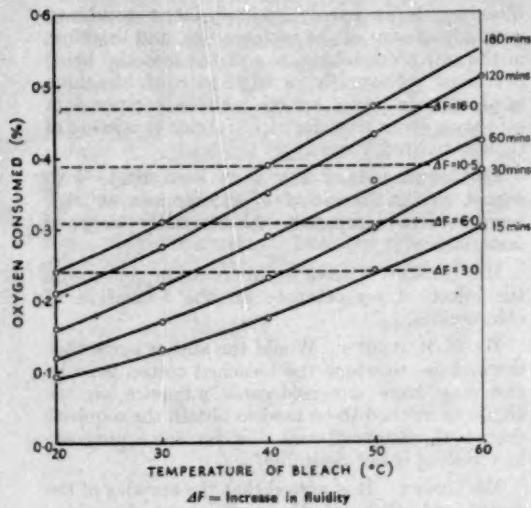
FIG. 7

The total quantity of available oxygen in solution was equivalent to 0·6% on the dry weight of yarn and the ratio of liquor to cotton was 20 : 1. The horizontal lines denote equal increments of fluidity. Thus a change in temperature of ±5°c. will cause a change in oxygen consumption of ±0·02% on 0·3% and a change in fluidity of ± 2 units about a mean value of 6 units, irrespective of the nominal temperature. Seasonal fluctuations of this order are by no means uncommon in bleach works.

Similar relationships to that shown in Fig. 7 are observed after scours of increasing severity, but the slopes of the curves and the amount of oxygen consumed per unit rise in fluidity decrease with the thoroughness of the scour.

The rate of oxidation of cotton cellulose increases by a factor of 2·7 for each 10°c. rise in temperature, and similar temperature coefficients have been found for mercerised cotton and viscose rayon. The difference between this value and the lower one (2·3) found to apply in bleaching is of little practical significance, because of the relatively high rate of the bleaching reactions. The rate of consumption of oxygen by mildly scoured cotton is, at the start of the bleach, approx. 180 times that for purified cotton cellulose.

* * *

The author would like to record his appreciation of the services of Miss C. Alvey and Mr. J. W. Duckworth, who carried out much of the experimental work.

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Discussion

Mr. H. A. TURNER: It is very surprising to see that this very simple relation between oxygen consumption and modification of cellulose is independent of temperature. The same thought seems to have struck Professor C. S. Whewell and myself, and we would like jointly to ask whether Mr. Derry has had any evidence that the bleaching efficiency shows a similar simple relation, i.e. between oxygen taken up and extent to which colouring matters are destroyed.

Mr. DERRY: The relation between oxygen consumption and quality of white for a given starting material is independent of temperature as far as can be ascertained from subjective assessment of whiteness. Reflectometers will, with care, give reliable estimates of brightness, but the quantitative measurement of the hue of near-white fabrics presents very great difficulty.

Mr. H. W. PARTRIDGE: Has the author any experience of the application of the principle to bulk production?

Mr. DERRY: The principles outlined in the paper have been applied successfully in the continuous processing of cotton and viscose rayon yarns and fabrics where the conditions allow of adequate control of concentration of bleach liquor and the temperature and duration of the treatment.

Dr. G. SCHWEN: Have any experiments been made on the influence of the temperature of bleaching on the fastness of dyed or printed material? This question seems to be of importance, not only to the bleacher when he has to bleach coloured goods, but also to laundries, where chlorination is often done— unfortunately— at elevated temperatures.

Mr. DERRY: We have examined the effect of temperature upon the rate of destruction of certain vat dyes, notably the indanthrones, which change from blue to green under the action of sodium hypochlorite. When fabrics containing such dyes are "bleached" for equivalent periods at 20°c. and 60°c. and pH 11 the effect on colour is approximately the same. The uncontrolled use of hypochlorite bleach liquors in laundries in this country is now largely a thing of the past. I regret to say that it is now the housewife who has discovered that brilliant whites can be obtained by the use of hypochlorite liquors (in their many proprietary forms) at elevated temperatures without control, but this matter is outside the scope of the discussion.

Mr. N. F. CROWDER: The results illustrated in Fig. 5 show that with a mildly scoured poplin the rise in fluidity is the same for a given oxygen

consumption at 20°c. and at 60°c. Has similar work been carried out on hypochlorite liquors nearer the neutral point, where a very rapid reaction may be expected, and would this be of interest in connection with the development of continuous hypochlorite bleaching processes?

Mr. DERRY: For the reasons given in the introduction of the paper, practically the whole of the work has been concerned with alkaline liquors buffered in the pH range 10–11. Although neutral hypochlorite liquors may have certain special applications, as, for instance, in linen bleaching, they have nothing to commend their use in the bleaching of cotton or viscose rayon. At pH 7 the proportion of available oxygen consumed in degradation of cellulose is greater than at pH 11, presumably because the bleaching reactions and those involved in oxidation of the cellulose are not equally accelerated by the increase in hydrogen-ion concentration.

Mr. J. RAYMENT: I would be interested to learn whether the white produced at 50°c. is equal in stability to prolonged storage to that produced by normal methods from a cloth prepared under the same conditions.

Mr. DERRY: Yarn specimens bleached to the same degree of whiteness at temperatures ranging from 20° to 60°c. appear to be equally resistant to discoloration after approx. 4 years' storage.

Mr. C. GARRETT: How would you overcome the difficulty of obtaining and maintaining uniformity of temperature with 3 tons of cold cloth coming from a washing machine containing a large amount of cold water that requires displacement before equilibrium and stability can be established?

Mr. DERRY: In order to maintain uniformity of temperature it would be necessary to raise the temperature of the cloth in the washing machine to that of the bleach liquor. An efficient saturator of the type employed in the du Pont peroxide bleaching range would ensure efficient replacement of water in the cloth by the hypochlorite bleach liquor. With this arrangement a small lagged Gantt piler or J box would be needed to allow the necessary time for bleaching. Although the highest temperature which can be used to bleach cloth in rope form may not be greater than 30° or 40°c., some form of automatic temperature control would be an advantage in that it would overcome the fluctuations in fluidity of the bleached cotton often caused by day-to-day and seasonal variations in the temperature of the water supply.

Mr. GARRETT: Would you propose to heat the solution with free steam or a multitubular heater?

Mr. DERRY: I have no views on the best material to use for heater pipes, but direct heating with steam through an easily replaceable perforated pipe is to be preferred to a multitubular heater, in which corrosion of welded joints might go undetected.

Dr. C. A. MUHR: Bleaching with hypochlorite at high temperatures is a very difficult process with which to get even results in bulk work.

Mr. DERRY: The prerequisite for uniform bleaching is an evenly scoured fabric combined with adjustment of the temperature, and therefore of the rate of bleaching, to suit the material being processed. Naturally, a high rate of bleaching is more appropriate for open cloths composed of soft-spun yarns than for close fabrics consisting of tightly twisted yarns.

Dr. MUHR: Have any tests been made with regard to the formation of chloramines at high temperatures compared with normally bleached material?

Mr. DERRY: I have no information concerning the effect of temperature on the formation of chloramines.

Mr. G. B. ANGUS: Would the author agree that the end-use to which the bleached cotton is to be put may have a considerable influence on the choice of method to be used to obtain the requisite degree of whiteness, and that for some purposes kier boiling is not desirable?

Mr. DERRY: It is agreed that the severity of the scour and that of the subsequent bleaching treatment should be related to the end-use of the fabric. Nevertheless, it is not justifiable to sacrifice the textile qualities of the fibre in order to save time in processing or to obtain a good but unstable white. It is our experience that, unless the non-cellulosic constituents of the cotton are removed as completely as possible in scouring, the permanence of the white and the absorbency of the cloth will not be as good as with a thoroughly scoured material.

Mr. R. W. SPEIRS: Side by side with the accelerated bleaching effect with rise in temperature there will tend to be an increased corrosion effect on plant employed. Has any work been done on this parallel question? One has in mind the effect, say, on stainless-steel equipment of sodium hypochlorite at 60°c., especially with sodium chloride present.

Mr. DERRY: It is, of course, impossible to generalise on the subject of corrosion. In general, the makers of stainless steel will not guarantee its use for hypochlorite liquors under any circumstances. Nevertheless, stainless-steel machines are very frequently used for bleaching without ill effects, and we have, at the B.C.I.R.A. and elsewhere, carried out trials with warm hypochlorite liquors without detectable damage to the equipment. Much depends on the care that has been exercised in fabrication, and the reputable manufacturers of textile-finishing machinery are at the present time producing equipment from the chemically more resistant steels which withstand the action of alkaline hypochlorite liquors extremely well. Of course, in no circumstances should acidic liquors containing free chlorine be used in such equipment.

Mr. D. A. DERRETT-SMITH: Has the Pad–Roll technique been applied to bleaching with warm sodium hypochlorite?

Mr. DERRY: Not to my knowledge. The advantages of a warm hypochlorite bleach are obtained in a fully continuous bleaching process in

which the duration of treatment can be accurately controlled. From Dr. Landqvist's description of the Pad–Roll system no advantage would appear to be gained from acceleration of the bleaching process.

Mr. S. BURGESS: In the discussion on the earlier paper by Crowder and White, it was stated in answer to a question that, whilst sequestering agents were not so necessary with hypochlorite bleaching as with peroxide bleaching, they might become so if iron were present or in linen bleaching, where copper is present. Does the present author agree, and which type of sequestering agent would he suggest?

Mr. DERRY: I would agree that the removal of trace metal impurities before hypochlorite bleaching is very desirable, although the consequences of such contamination are far less serious than in peroxide bleaching. Sequestering agents will effectively remove traces of copper and iron picked up from the water supply or from the chemicals used in the scour, but they are of little value in dealing with very resistant stains, which are invariably those that have found their way into the yarn before and during weaving. These often consist of a mixture of finely divided metal with oil and dirt, and no single treatment can be recommended for dealing with them.

The Pad–Roll Dyeing System

C. O. Eriksson, N. Landqvist*, and B. Mellbin

A brief discussion is given of the Pad–Roll system. The dyeing machine, comprising a padding device, an infrared heating zone, and a batching chamber in which constant atmospheric conditions can be maintained, is described. The composition of the direct dye pad solutions is discussed with special reference to dyes and addition of electrolytes, and the pre- and after-treatments of the fabrics are considered. Finally, the laboratory dyeing mehods applicable to the Pad–Roll system are given.

INTRODUCTION

The established continuous and semi-continuous methods of open-width dyeing with direct cotton dyes, notably the pad–steam and pad–jigger methods, give relatively good penetration of the fabric, but often the resultant dyeings have inadequate wet fastness. This is due to the insufficient time allowed for dye diffusion, so that the fibres are only "ring-dyed". It is clear that maximum wet fastness can be achieved with each type of dye only if "dyeing-in" times are permitted which correspond roughly to a true equilibrium between the dye in the fibres and that in the solution. A possible method would be to dye on the roll, but there are practical difficulties. To avoid substantivity effects it would be necessary in most cases to pad at a low temperature. Since such a temperature very often would be unsuitable for the actual dyeing process, the padded fabric ought to be heated. The heating must be carried out under such conditions that no disturbances of the liquid phase occur, and the same requirements are also needed for the dyeing-in period.

The Pad–Roll system has been evolved to meet these requirements.

PRINCIPLE

In principle, the material is padded with dye liquor at a suitable low temperature in a small trough, and passed into a chamber where it is heated to the required dyeing temperature, without any change in the padded liquid, by means of infrared radiation. The fabric is wound loosely on a large-diameter roll, which is then rotated slowly for a time sufficient to permit uniform distribution of dye in the material. The cloth is then removed for drying or rinsing and after-treatment.

DYEING MACHINE

The fabric first passes a stretching device, to keep the tension constant, and then a pair of guides before it reaches the impregnation trough. The trough is fitted with a water jacket, and the water, and hence the dye liquor in the trough, are kept at a constant temperature by means of a thermoregulator, which controls the amount of steam blown into the water. The jacket is also fitted with an overflow device, which drains off the increased volume of water due to the condensation of steam. The volume of the trough is of the order of 10 litres for machines designed for narrow-width fabrics, and the entire volume of dye solution is renewed within 1–2 min. at normal

running speeds. In order to get as good impregnation as possible before the fabric reaches the nip of the padder, this small volume is combined with a comparatively long path through the padder trough. This is arranged by filling up the trough by a displacing device. A constant level is maintained by means of a device regulating the flow of dye liquor from a tank maintained at the same temperature as the trough. To facilitate preparation of dye liquor in the tank, a pump is provided, which can be used also for continuous circulation of the tank solution so as to maintain its homogeneity, as well as for mixing in connection with dilutions. For obvious reasons this circulation should not include the padder trough, since otherwise the entire volume of the dye liquor would be available to produce undesirable substantivity effects, and the advantage of using a small padder trough would be lost.

As in the case of all padders for continuous dyeing, the most important requirements are uniform squeezing, and also ability to attain this even with a light squeezing effect: for deeper colours the limited solubility of the dyes sometimes necessitates a comparatively large pick-up.

After having gone through the padder and a compensator for regulating the batching motor, the fabric passes into the preheating zone, where it is heated to the desired dyeing temperature by means of electrically produced infrared radiation acting on both sides of the fabrics. The maximum power input is of the order of 40 kw. Another possible method of generation of infrared radiation would be to burn gas in tubes; the radiation is emitted from their outer surface. The entrance to the infrared heating zone is a narrow slit, preventing any considerable transport of air into this zone, which would disturb the constancy of the atmosphere and the temperature of the fabric. This temperature is, of course, controlled by the wet-bulb temperature of the surrounding atmosphere.

From this section the fabric reaches the batching chamber. Two different types of machine are in use, one with a stationary chamber, the other with a detachable one. Since the latter type gives as good results as the first, the detachable-chamber type may be that used in the future. The detachable chamber can be taken away from the padder and the heating zone, sealed, and stored at any convenient place during the "dyeing-in" period. Thus another chamber can be fitted and a new run started during this period, so that very high production can be obtained. In the chamber the
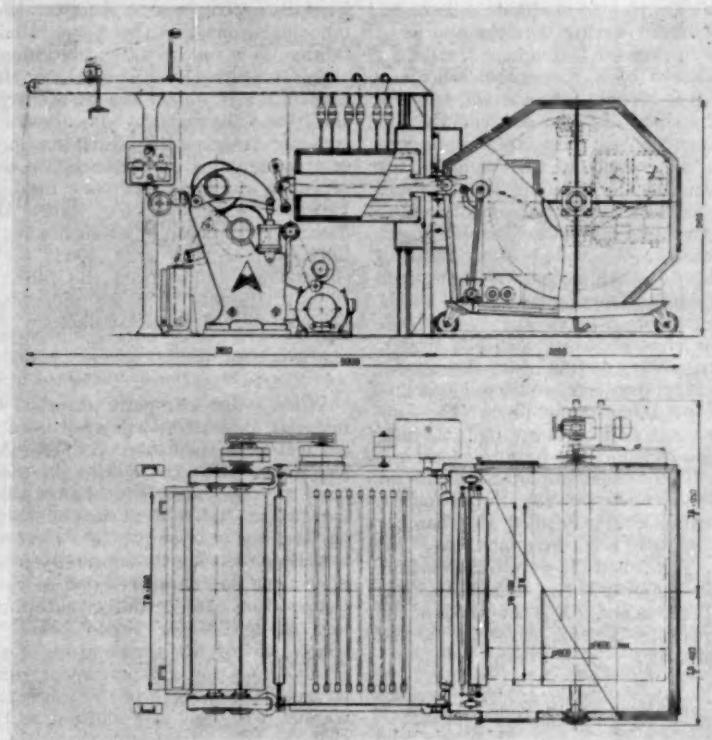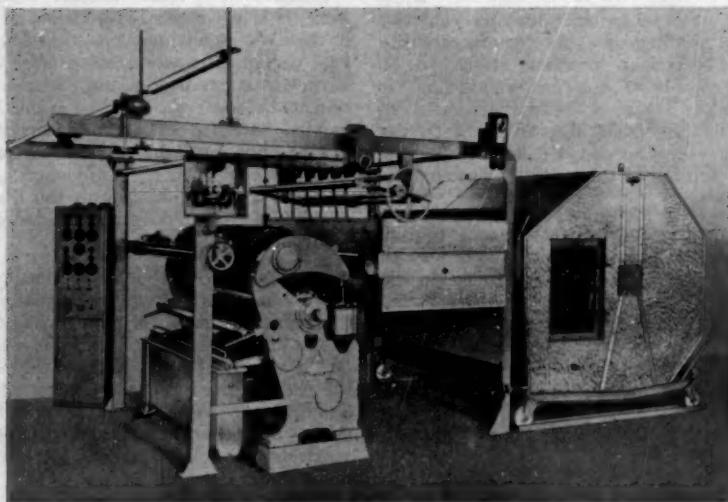

Fig. 1

Fig. 2

Fig. 1 and 2— Detachable-chamber Type of Machine

fabric is wound upon a drum having a comparatively large diameter, to give moderate differences in speed of revolution during winding and only small differences in pressure throughout the batch. The fabric is touched by a "pendulum roller" at the point where it is brought into contact with the roll; this and the short distance between the nip and the batching roll will keep the fabric free from wrinkles. By means of the compensator previously mentioned, the speed of the batching motor is controlled so that a minimum of tension is applied to the fabric. After batching and closing the chamber, the roll is kept rotating slowly by means of a small motor. This prevents any change within the liquid phase of the batch, which would be dangerous before the dye is fixed. The walls of the chamber are electrically heated (via a thermoregulator) to maintain the atmosphere at constant temperature, and small amounts of steam are blown into the chamber. The flow of this steam is controlled by a wet-bulb thermoregulator, giving a constant wet-bulb temperature, which seems to be the most important factor for controlling the constancy of the liquid phase. When the dyeing-in period is finished, the chamber is taken to a dryer, or to a machine for rinsing and aftertreatment. Fig. 1 is a diagram of a machine of the detachable-chamber type. The dimensions are given in millimetres and TB is the width of the fabric to be treated. Fig. 2 shows an actual machine of this type.

PRETREATMENT

As in all continuous dyeing processes, the pretreatment of the fabric is of the greatest importance. With delicate fabrics a treatment at open width is preferred, but in many cases the rope form will give satisfactory results.

It may also be mentioned that the Pad–Roll machine has proved to be suitable for some pretreatment operations, e.g. desizing, chlorite bleaching, and boiling off. As regards chlorite bleaching, the corrosion problem seems to be practically negligible if the entire machine is made of stainless steel: no corrosive action of chlorine dioxide has been observed. Since the padder trough solution can be kept cold, the likelihood of corrosion at this point is also remote.

If the width of a rayon fabric increases considerably during padding, this effect may require the fabric to be dried to a greater width than that obtained by completely slack drying conditions. Otherwise, difficulties may arise from this increase, e.g. from wrinkles passing the pad nip. However, loop-dried rayon fabrics can often be processed without any trouble. Independently of the method of drying, it is necessary to keep the residual moisture content low: uneven drying may give rise to differences in actual dye solution pick-up.

Sewing up the different pieces of a run can also be regarded as part of the pretreatment. Since the Pad–Roll method involves a liquor ratio of approx. 1 : 1, and the dye solution is not replaced during the dyeing-in period, the sewing-up has to be done carefully. The reason is that the material is inhomogeneous at the seam, and on delicate fabrics this can cause marking-off problems, owing to differences in the amount of solution absorbed and differences in affinity between the thread and the material to be dyed. In the case of cotton and rayon staple fabrics these problems are not of great practical importance, but in the handling of e.g. a rayon taffeta they need consideration. However, experience has shown that such undesirable effects can be avoided when the seams are butt-sewn on the grey goods and the sewing threads are taken from the fabric to be dyed. Finally, the use of nylon monofilament threads has also proved to be satisfactory.

PADDING

When a dye is rapidly absorbed by the textile material, difficulties will arise from concentration changes in the pad solution due to this absorption. The depth of colour, and in the case of dye mixtures the hue also, will change during the run. In the Pad–Roll system such effects are minimised by keeping the temperature of the dye solution low, thus reducing the rate of dyeing. This can be done since the fabric is heated to a suitable dyeing temperature after padding, substantially without any change in the liquid phase. Despite the comparatively low temperature of padding (often about 40°C.), good impregnation can be obtained, as a sufficient length of the fabric is brought into contact with the pad solution in the trough, so that the time of rewetting is comparatively long. The trough volume is, as previously mentioned, small, thus compensating for the long time of contact, since the pad solution is rapidly consumed. This is also favoured by a high pick-up and a high running speed.

A high pick-up is also desirable with deep colours, since the depth is partly controlled by the solubility of the dye. A change of pick-up from 80 to 100% will permit a corresponding increase in depth. However, it has been found that a kind of "emulsion technique" can often be applied. The dye is padded as a dispersion, and owing to the long dyeing time available this dispersion is brought into solution when the proportion of dye present in true solution diffuses into the fibre, i.e. as the concentration of dye in the padded solution tends to decrease.

From the above it is found that a high running speed ought to be used. The maximum speed is controlled by the rate of rewetting and the capacity of the infrared heating, the latter being a function of the weight of the fabric, the temperature of the the pad solution, and the dyeing temperature to be obtained. With a medium-weight rayon staple fabric in the machine previously described, the maximum padding speed is of the order of 60 metres/min.

Although high pick-up is generally desirable, some fabrics need to be well squeezed. Since the pad liquor is held in the yarn by capillary forces,

an excess of dye liquor can move during the dyeing-in period. This is sometimes the case on taffetas, and would result in an uneven dyeing. A high squeezing effect is also desirable when the textile material itself is uneven, since greater uniformity of distribution of the padded solution on the fabric is obtained. Further, the low liquor ratio decreases the tendency to dye transfer between parts of different affinity.

The distance between the nip of the padder and the entrance to the infrared heating zone is made as short as possible, but at low running speeds slight evaporation cannot be avoided. Such evaporation will cause an increase in the concentration of the dye liquor at the surface of the fabric, and possibly precipitation of dye. If the precipitate is not brought into solution during the dyeing-in period, this will cause a decrease in the brightness of the colour, and sometimes a "two-sided effect". From the practical point of view improvements can be obtained if the fabric is carefully rinsed after dyeing, and although phenomena of this kind occur only with a very small number of dyes, they have to be taken into consideration. However, they can be completely controlled if no salt is added to the pad liquor, but small amounts of an emulsifying agent of e.g. the non-ionic type.

DIRECT DYE PAD SOLUTION

In all dyeing processes with direct dyes, including padding, dye selection is known to be of importance, and often only a narrow range is available. Since in the Pad–Roll machine the padded fabric is heated substantially without change in the liquid phase and the dyeing-in period may be quite long, practically all direct dyes can be used. The long dyeing-in period reduces the need to add electrolytes to the dyebath, and this means that comparatively concentrated solutions can be used without any difficulties. If normally the maximum depth of colour is controlled by the solubility of the dye, the "emulsion technique" can often be applied above this limit.


Fig. 3—Conductivity Measurements at 95°c.

The effect of electrolytes on concentrated solutions of direct dyes has not previously been investigated to any considerable extent. However, conductivity studies (Landqvist, unpublished results) in the temperature range 20–90°c. on a number of dyes in practical use gave some interesting results. It was found that even at high temperatures it often happens that the added electrolyte is to a great extent taken up by the dye aggregates, so that only a very small amount is available for increasing the rate of dyeing, i.e. for lowering the potential barriers. Thus, an addition of electrolytes would in some cases actually have an unfavourable effect by decreasing the rate of dyeing. Results from dyeing practice have confirmed these results. An example of this behaviour is given in Fig. 3, which shows the influence on the conductivity of sodium chloride additions of two different direct dyes at a concentration of 20 g./litre and at a temperature of 90°c.

An addition of electrolyte is obviously of value with a dye of low aggregation tendency at the dyeing temperature. If a dye is sensitive to "precipitation" as discussed above, no salt or other electrolyte can be added. Between these limits no general comments can be given about the use of electrolytes. However, experience has shown that 80% of all dyes can be used without addition of any salt, even up to deep colours. If a laboratory dyeing, made in order to match a shade, shows that the rate of dyeing or the final equilibrium is unfavourable, further dyeings of that kind, with increasing amounts of electrolytes, will give the information needed for the choice of a proper pad solution composition.

INFRARED HEATING

The heating must be uniformly distributed, otherwise the solution phase may be disturbed, which may cause uneven dyeing.

At the beginning of the run the wet-bulb temperature of the heating zone and the chamber is adjusted to the dyeing-in temperature required. During the run, the energy input is regulated to keep the wet-bulb temperature constant. Condensation or evaporation is thus effectively avoided, and the liquid phase maintained constant. Careful control of this part of the process is very important; evaporation is not necessarily dangerous, but condensation seems to be so, causing uneven dyeing or "two-sided" effects. The dry-bulb temperature of the chamber is not of the same great importance, and is normally kept some degrees above the wet-bulb value.

The dyeing-in temperature depends on the dye, the composition of the liquor, and the fabric to be dyed. Generally, it should be as high as possible. However, higher temperatures require more careful control of the conditions of the atmosphere in the chamber, since the system grows more and more labile with rising temperature, owing to the increase in heat transfer and tendency to migration.
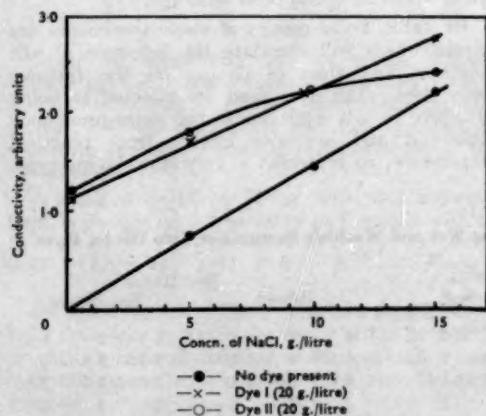
High dyeing-in temperatures are valuable in spite of the long dyeing times because the reduced absorption forces and the increased rates of diffusion within the fibre permit the dye molecules to enter parts of the fibre where the absorption forces are greatest.

The temperature range used in practice is, in the case of direct dyes on cellulose fibres, 85–90°c.

BATCHING

The padded and heated fabric is batched in the chamber, and in this part of the process three requirements ought to be fulfilled. The batch should be as perfect as possible; i.e. the selvedges should be in a straight line. The batch should also be free from wrinkles. The third requirement, which is quite important, especially with rayon fabrics, is that the tension must be very low. Not only the handle of the fabric is affected by the tension: with the same proportion of adsorbed dye on the fabric an increase in tension from 0 to 5 g. per cm. on a 100-g./sq.metre rayon staple fabric may in some cases reduce the optical colour yield by as much as 50%.

DYEING-IN PERIOD

Although no change in the liquid phase is still essential during the dyeing-in period, a small difference between wet- and dry-bulb temperatures will not cause any disturbances, and is of advantage, since condensation and any resulting dripping from the ceiling of the chamber are avoided. During the dyeing-in period no control is needed, since the conditions of the chamber atmosphere are regulated automatically.

Since maximum dye absorption is attained asymptotically, the time of dyeing is primarily determined by the fastness required and/or by the need of being so close to equilibrium that no differences in colour can be observed between the beginning and the end of the run. Surprisingly, the fastness is the important factor: identical colours are normally obtained within shorter dyeing times. The time required is easily found from laboratory dyeings, and varies from 1 hr. for pale colours to 8 hr. for very deep colours, for direct dyes on cellulosic fibres. However, the dyeing time is also greatly dependent on the properties of the dye used, and for some dyes maximum fastness also can be obtained within 1 hr., even with comparatively heavy dyeings.

One of the disadvantages of continuous dyeing processes is that generally long runs are needed for economic use. The Pad–Roll system, however, also allows short runs to be made. This is attained when a run is made from light to dark colours, and the padder and the guiding rollers are cleaned between each colour. A piece of fabric, preferably that to be dyed, is sewn between each part of the run, separating the different colours. The length of this piece ought to be sufficient to prevent any "bleeding" between the different layers of the batch, viz. about 20 metres. Another possibility is to use a rubber-coated fabric to separate the layers.

AFTERTREATMENTS

After the dyeing-in period, the chambers are moved to machines for further treatments. In the case of light and medium depths, the fabric can often be dried immediately after dyeing, since all the dye is absorbed. However, some dye impurities or added electrolytes sometimes make rinsing necessary, e.g. when the fabric is to be given a crease-resistant treatment afterwards, and these substances would affect the process.

If an aftertreatment is to be given with a dye-fixing agent, this, as well as the rinse, can easily be done on an open-width washer, a jig, or a winch machine. It has been observed that a treatment made in rope form is not very dangerous as regards wrinkles if the complete dyeing-in has been made in open width. Other treatments, e.g. diazotisation, can also be made on a jig. Surprisingly, the handle of a rayon fabric is not very much affected by this, probably because the treatments are carried out at low temperatures.

FASTNESS AND COLOUR YIELD

The long time of dyeing enables maximum fastness of the dye to be obtained, and experience has shown that the same or better fastness than given by winch dyeing is a normal result of Pad–Roll dyeing. The colour yield, being a function of the small liquor ratio and the very good exhaustion, is better than that obtained by jig and winch dyeing. This is especially the case when dyeing deep colours, and an increase in colour yield up to 25% has been observed.

In Table I the results of two experiments are given, which will elucidate the influence of salt addition and time of dyeing on the fastness properties. The dyes used are selected as being sensitive to salt additions in the sense previously discussed and are also known, from practical experience, to represent a very slow-dyeing type.

TABLE I

Influence of Salt Additions and Time of Dyeing on the Wet and Washing Fastness of Two Direct Dyes

Concn. of NaCl (g./litre) ...		0	5	15	0	5	15	0	5	15	0	5	15
Fastness Test Temp. (°c.)	Time of Dyeing (hr.)	Dye I						Dye II					
		Rinsed			Not Rinsed			Rinsed			Not Rinsed		
20	1·0	3·5	3	3	1	1	1	4	2	2	2	2	1·5
20	2·5	3·5	3·5	3·5	2	2·5	2	4	4	3·5	2·5	2·5	2
20	5·0	4	4	3·5	1·5	1·5	1·5	4·5	4·5	4	2·5	2·5	2·5
40	1·0	1·5	1	1	1·5	1	1	1	1·5	2	2	1	1
40	2·5	2	1·5	1	1·5	1·5	1·5	3	2·5	2	2·5	2	2
40	5·0	3	2	1·5	1·5	1·5	1·5	3	2·5	2	2·5	2·5	2

In order to obtain the proper fastnesses, 4 (E.C.E.) in a 40°c. wash, about 10 hr. of dyeing without salt is required. The dyeings were made on a laboratory dyeing machine which is a small-scale model of the Pad–Roll machine used in practice. The pad solution contained 20 g. of the dye per litre and the amounts of sodium chloride given in the table. The padding temperature was 50°c. and the pick-up of the medium-weight rayon-staple fabric to be dyed was 100%. After the dyeing-in period at 85°c., half of the fabric sample was rinsed in water at 20°c. for 1 hr.; the other part was dried at 40°c. without rinsing. No aftertreatment was given.

In these experiments it was found that for each salt concentration the proper shade was obtained within 1 hr. of dyeing, and no further change occurred when the time was increased. However, increasing salt concentration caused a decrease in the brilliancy of the colour.

OTHER DYES AND TEXTILES

A great number of direct dyes have been used for dyeing millions of metres of cellulose fabrics. Other dye classes and materials have only been subject to experimental dyeings, and the results can be summarised as follows—

The dyeing of acetate rayon and nylon with disperse dyes has, as far as experiments show, been successful. However, the dispersing agents ought to be carefully selected, though e.g. the non-ionic type seems to be generally applicable. For dyeing deep colours addition of a thickener to the pad liquor is advantageous, since it will increase the solution pick-up and keep the dispersion stable. Also water-soluble acetate-rayon dyes have been used for nylon with very good results.

It may also be mentioned that cross-dyeing of acetate–viscose rayon has been very successful, and the acetate reserves on acetate–viscose rayon staple mixtures are mostly better than the corresponding winch-dyeing results.

Finally, the results on wool with e.g. acid dyes suggest that the Pad–Roll system might be used for wool piece dyeing.

COLOUR MATCHING

Since no corrections can be made during the dyeing, a simple and reliable laboratory dyeing method is necessary for any continuous dyeing method. In the case of the Pad–Roll system the following laboratory dyeing technique seems to be satisfactory—

A small strip, about 15 cm. wide and 200 cm. long, is padded on a laboratory pad mangle with a dye solution which is expected to give the shade required. The trough of the mangle is in principle similar to that of the Pad–Roll machine; i.e. the padding can be made from a small volume at the desired temperature. The speed of the padder is such that the immersion time is substantially the same as that selected for the large-scale run. The pressure on the bowls is chosen so that the pick-up is the same as that obtained in practice.

After padding, the fabric is batched on a stainless-steel tube and wrapped in a piece of plastic, e.g. polyethylene sheet. The roll is then put on one of the pins of a moving wheel, which is situated in a small chamber fitted with temperature controls.

Within the limits needed for a good colour matching, a dyeing time of about 1 hr. is generally sufficient. After the dyeing-in the wrapped sample roll is allowed to cool down at room temperature for about 1 hr. before unwrapping. The strip is then treated in the same manner as the bulk of the fabric.

This laboratory dyeing technique can be applied, not only for the purposes mentioned above, but also for investigations of the influence of the dyeing time on the fastness.

ECONOMICS

Although the economics of the Pad–Roll system can be of great interest, this will not be discussed in this paper, as an analysis of this subject has already been given [1]. It has been shown that the system compares favourably with e.g. winch dyeing even on the basis of increase in production per man-hour.

Finally, it must be stated that the Pad–Roll system is no general solution to all dyeing problems. However, in many cases great improvements are obtained as compared with other dyeing methods, and future work will show the limitations of the method as well as new possibilities with new ranges of dyes and fibres.

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    RYDBOHOLM
    SWEDEN

References

[1] Eriksson, C. O., Landqvist, N., and Mellbin, B., *Textil-Rund.*, **10**, 51 (Feb. 1955).

[2] Wegmann, J., *J.S.D.C.*, **71**, 777 (Dec. 1955).

Discussion

Mr. K. S. LAURIE: There must be a considerable time difference between the entry of the first end of cloth on the roll and that of the last end. Does this difference in treatment give rise to any trouble?

Dr. N. LANDQVIST: As mentioned in the paper, the time needed to obtain the proper fastness considerably exceeds that needed for equal depths. Thus, such differences do not occur.

Mr. LAURIE: I note that care has been taken to keep the infrared heating even and low in intensity. In spite of this, is there no trouble due to migration of dyes to the surface of the fabrics?

Dr. LANDQVIST: It is essential to maintain the heating conditions such that migration to the surface is prevented. By controlling the wet-bulb temperature such disturbances can be easily avoided, as described in the paper.

Mr. W. PENN: Is it possible to prepare goods in rope form for dyeing on the Pad–Roll system, or is open-width preparation essential?

Dr. LANDQVIST: It is possible to prepare goods in rope form, but for more delicate fabrics open-width treatment is recommended. It is also recommended for another reason: such treatment mostly means increased production in the pre-treatment operations.

Mr. N. F. CROWDER: Can the machine be used for bleaching on the Pad–Roll system with sodium chlorite or with peroxide? In the case of the former, is there any corrosion of the stainless steel equipment?

Dr. LANDQVIST: The machine is successfully used for chlorite bleaching, and no corrosion appears if the whole equipment is made of stainless steel.

The small number of laboratory experiments on peroxide bleaching have not been a success: the tendering effect has been too great. This is probably due to the high concentration needed and the long bleaching time. Better stabilisation of the peroxide may give improved results.

Mr. J. K. SKELLY: Does the preferential uptake of water by the dry cloth entering the pad box cause a slight change in the concentration of direct dye and give a length of cloth off shade at the beginning of a run? If so, firstly, what length of cloth may be expected to be off shade? Secondly, is it necessary to use a dye feed liquor of different concentration from the dye liquor in the pad box to prevent ending?

Dr. LANDQVIST: Owing to the design of the padder trough, the moderate impregnation temperature, and the high running speed, ending can be practically completely avoided. However, it is recommended that the trough should be filled up just before the actual fabric enters it, and that the machine should then be brought up to full speed immediately. Runs where the fabric is slightly off-shade for more than 4 metres are not normally observed.

Mr. SKELLY: Is it recommended to use dyed or undyed leaders for each dyeing? If dyed leaders are used, is it necessary to keep a stock of leaders dyed in different colours?

Dr. LANDQVIST: Since the transfer of dye between different layers of the batch is very small, either dyed or undyed leaders can be used. It is not necessary to keep leaders dyed in different colours in stock; however, heavily dyed leaders are not recommended when dyeing pale colours.

Mr. C. HOBDAY: Have any experiments been carried out on the dyeing of continuous-filament nylon fabrics with neutral chrome-complex dyes? If so, what degree of coverage of the irregular nylon has been obtained?

Dr. LANDQVIST: As far as I know, no large-scale experiments have yet been made with neutral chrome-complex dyes.

From laboratory dyeings it might be concluded that improved dyeing results can be obtained on irregular nylon.

Mr. C. P. ATKINSON: The authors claim that this very interesting process is essentially continuous. In the pad–steam method of applying direct cotton dyes, the usual time for steaming is 4–5 min. — one author in a previous paper [2] has even stated that with certain selected direct dyes a time of only 2 min. is necessary. As the authors refer to a "dyeing-in period" of 1–8 hr. in the Pad–Roll system, (a) why is this long period necessary; (b) what are the advantages of this procedure; (c) on what basis does the Pad–Roll system compare favourably with the continuous pad–steam technique?

Dr. LANDQVIST: (a) and (b) For practically all textile dyes, the dyeing mechanism includes a change in the energy of the dye molecules as a primary effect: this is the force that brings the molecule from the dye solution to the fibre phase. However, for a great number of dyes this change in energy is also responsible for the fastnesses obtained in practice. The dye transfer from the bulk of the solution to the fibre surface can be increased by mechanical means; the transfer from that surface to the fibre phase is affected only by the composition of the dye solution and by the temperature. If a textile material could be regarded as completely homogeneous, the solution to the problem would be to keep the dye activity at the fibre surface as high as possible, i.e. to use mechanical means to increase the transfer from the solution to the fibre surface. Unfortunately, no textile material can be regarded as completely homogeneous, and a level dyeing is not easily obtained. Thus, in the search for better dyeing methods an even initial distribution of the dye has frequently been used: the fabric is padded and then given one or another kind of "dye fixation" treatment. Great improvements as regards level dyeing have been made in this way, but the method entails some disadvantages, since the rate of dyeing is comparatively low. Of course, some dyes will within a few minutes reach an even distribution throughout the fibre, but such dyes often have the disadvantage of also diffusing rapidly in the opposite direction when the textile material is later on brought into contact with wash solutions. Other dyes, which have a very high affinity for the fibre, can show comparatively good fastnesses even after short times of dyeing, although the distribution of the dye in the fibre can be regarded as a kind of "ring dyeing". However, if the same amount of the dye were evenly distributed throughout the fibre cross-section, better fastnesses might be obtained, since the concentration difference between the fibre surface and the surrounding solution would then be decreased.

Another possibility, which is not very often considered in discussions of dyeing mechanism, is that the adsorption energies at different points of the fibre are probably different. Thus, a cross-

section analysis would not give complete information, since an even distribution may not prove that maximum adsorption forces are active: the time needed for such maximum adsorption may exceed that for even distribution.

(c) Some of the advantages are—

  (i) The long dyeing time available

  (ii) The very low tension applied to the fabric during the dyeing operations; i.e. the handle of the fabric is very little affected by the treatment

  (iii) Practically all direct dyes are suitable for Pad–Roll dyeing

  (iv) The possibility of dyeing heavy depths in practically all colours

  (v) Short runs can be made without any considerable decrease in production

  (vi) A small, simple, and cheap dyeing machine

  (vii) The dyeing machine is easy to clean and simple to operate.

Mr. A. S. FERN: How many "dyeing-in" chambers are required in order to maintain an overall production rate of, say, 50 metres/min. when dyeing a deep colour (8-hr. dyeing-in period) on 100,000 metres of fabric?

Dr. LANDQVIST: The "circulation" time of the chambers will, under the conditions mentioned, be of the order of 10 hr. (padding + dyeing-in + aftertreatment). If we base our calculations on a

medium-weight fabric, we have about 2,500 metres in each chamber, i.e. we need about 1 hr. for the padding period. Thus, 10 chambers are sufficient if 3 shifts are assumed. (The amount of fabric is not important when it exceeds 30,000 metres, since this is the 10-hr. production.)

However, with a production of the order suggested in Mr. Fern's example, larger chambers might be recommended. The size mentioned here has been chosen with regard to average production conditions and with regard to the movement of the chambers.

Mr. H. W. PARTRIDGE: Does this process offer any advantage over normal methods in the production of solid dyeings on fabrics containing yarns of varying dyeing properties?

Dr. LANDQVIST: Since the transfer of dye between different parts of the fabric is small and long dyeing times are used, it does offer advantages. However, if the irregularities are due to differences in the optical colour yield, caused by differences in the physical structure of the cellulose fibre, it does not.

Dr. C. A. MUHR: I want to congratulate the authors on the emulsion technique for obtaining heavy dyeings. It is a big advance in the application of direct dyes to cellulosic materials to be able to dye practically all depths with the same fastness properties as a winch-dyed fabric.

A Modern Approach to the Raising of Textile Fabrics

C. S. WHEWELL

Methods of assessing the effectiveness of raising are discussed, and these are used to express quantitatively the part played by cloth construction and conditions of raising (pH, presence of lubricants and salts, etc.) in determining the response of a fabric to raising. Emphasis is laid on changes in thickness, tensile strength, and pile composition produced during raising.

Raising is one of the oldest of textile-finishing operations, and is the key process in the production of a wide range of fabrics, including blankets, flannelettes, and industrial fabrics. Although it was originally carried out by hand, the modern method of raising is to use a card wire machine or a teazle gig in which teazles are mounted on the surface of a cylinder. A great deal of attention has been paid to the development of card wire raising machines, and in their modern form they are efficient and capable of producing a wide range of styles. Until comparatively recently raised fabrics were made of wool or cotton, but the increasing production of staple rayon and nylon has given new impetus to the raising section of the industry, for extremely attractive styles may be obtained when suitably designed cloths are raised either wet or dry. Card wire machines formerly used for raising cotton or wool have been found to be suitable for producing many of the new styles, and even the teazle gig is not without its value as a means of obtaining interesting finishes on fabrics containing man-made fibres.

Although much thought has been given to the design of raising machinery, little work has been carried out on the more quantitative aspects of the raising process, and to remedy this state of affairs a systematic study of the process was initiated some time ago in the University of Leeds. The present paper is an account of some of the results obtained.

Experimental Methods

One of the difficulties in studying raising is to develop a satisfactory method of assessing raising efficiency. It is of course possible to measure the power consumed by the machine as it raises the cloth, but this has been rejected as too insensitive. The method can be used very effectively, however, if the raising machine is adequately instrumented. Four other methods have been used successfully. In the first [1] the resistance offered by a fabric to the points of a raising agency is measured. The instrument consists of a pendulum mounted on a ball-bearing and carrying at its extremity a steel comb which serves as a means of raising the cloth. When both pendulum and comb are hanging vertically the pattern of cloth to be raised is placed under the tip of the comb so that the teeth just touch the cloth surface. The pendulum is lifted to one side into a horizontal position and the cloth is lifted by 0·1 in. The pendulum is then allowed to fall, and the work done in raising fibres from the surface of the cloth is indicated by the height to which the pendulum rises after having passed through the cloth or by the number of swings required to bring it to rest. Generally the latter method was used.

The other methods involve measuring certain properties of the cloth before and after raising. In one [2] the actual weight of pile is measured by removing the surface fibres by means of a calibrated cutting machine, a special technique being adopted to reveal when all the pile has been removed and the machine is cutting into the body of the cloth. The second method is the simpler, although it is not always satisfactory when dealing with fabrics having a laid pile. It consists in measuring the thickness of the cloth before and after raising, the measurements being made at the comparatively low pressure of 1 g./sq.cm. Complete thickness–compression curves have been obtained in many cases, as a detailed study of the shapes of these curves is often useful in revealing differences in the weight and the type of pile. In other cases the loss in tensile strength of the weft yarns during raising has been measured, as it has been shown [3] that, on one raising machine at least, there is a linear relationship between loss in strength and pile production in the early stages of raising.

All these methods have proved to be useful, but one serious limitation has to be recognised. It has not been possible to control a commercial raising machine so that accurately reproducible results can be obtained on successive runs. This has meant that experiments have to be designed in such a way that several cloths are raised at the same time, and are therefore subjected to the same mechanical treatment. This has seriously limited the type of experiment which can be done, and it has not been possible to study the effects produced by altering machine settings and conditions. This work will eventually be undertaken, but it is necessary to use a specially designed and controlled raising machine. The methods available have, however, yielded interesting results, which demonstrate quite clearly the large number of factors, other than machine settings, etc., which can affect the susceptibility of a fabric to raising.

1. MECHANISM OF RAISING

The most obvious change brought about during raising is that the cloth becomes thicker owing to the production of a pile. This is done by pulling fibres from the fabric, and consequently the strength of the cloth falls. It is clear that the pile may be formed either by breaking fibres or by disorganising the yarns so that the ends of the

fibres are lifted out of the cloth. There are, however, no data which show the extent of these changes, and consequently several cloths were made from different fibres and raised together on a card wire machine. Measurements were made of the thickness of the fabrics, and the average length of the fibres in the weft after the fabrics had been subjected to increasingly severe raising treatments. The experimental details are given in Table I.

TABLE I
Composition and Construction of Fabrics

Type of Cloth	Count (worsted) Warp	Weft	Threads/inch Warp	Weft
Nylon	2/12·4	2/11·7	23	22
Bright Fibro ...	2/12·2	2/11·6	25	24
Matt Fibro ...	2/11·8	2/11·7	24	24
Rayolanda ...	2/12·3	2/12	23	22
Wool	2/12·4	2/12·2	24	23
Acetate rayon ...	2/12·5	2/12·3	24	22

Raising

Since it is technically impossible to reproduce raising conditions precisely, the fabrics were sewn together to form a single length, and this was run through a Tomlinson Q-Vee raising machine for various times at different gearbox settings. Raising was carried out in five stages (see Table II). A strip of fabric was taken from each of the six samples after each successive stage of raising, and measurements were made of the tensile strength of the weft yarns, the thickness and the bursting strength of the cloth, and the length of the fibres in the weft yarns.

TABLE II

Raising Stage	Setting of Machine, etc. No. of Rounds	Gearbox Setting
1	35	3·5
2	+10	4·0
3	+10	4·5
4	+ 5	5·0
5	+ 3	5·5

Determination of Fibre Length

Weft threads were carefully extracted from the sample, care being taken not to break fibres which had become entangled with those of an adjacent pick. The twist was taken out of the yarn, and the lengths of the individual fibres were determined by extending the fibre between tweezers to remove the crimp and then holding it against a millimetre scale. Sufficient fibres were measured to give an average value with an error of less than 5%.

Results

Table III shows that in all cases the average fibre length falls as the raising proceeds, and there is an approximate relationship between the reduction in fibre length and the increase in thickness. This reduction in fibre length is least with nylon and greatest with acetate rayon, the other fibres lying between these two extremes. Reduction in fibre length appears to be a feature of raising, and the data suggest that the raising machine functions by breaking fibres rather than by lifting them out by their ends. The rate of reduction would appear, from other experiments, to fall as raising proceeds, and it is possible that

TABLE III

Raising Stage	Cloth Thickness (cm.)	Reduction in Fibre Length (%)
	NYLON	
0	0·102	0
1	0·110	4·7
2	0·250	13·5
3	0·371	39·6
4	0·430	65·7
5	0·548	65·9
	BRIGHT FIBRO	
0	0·118	0
1	0·172	32·3
2	0·346	65·8
3	0·442	73·6
4	0·565	83·6
5	0·617	86·3
	MATT FIBRO	
0	0·115	0
1	0·175	41·2
2	0·404	59·6
3	0·526	78·8
4	0·578	80·5
5	0·620	84·9
	RAYOLANDA	
0	0·112	0
1	0·141	17·2
2	0·267	42·2
3	0·403	69·2
4	0·540	77·1
5	0·600	81·0
	WOOL	
0	0·189	0
1	0·226	21·5
2	0·348	40·0
3	0·632	60·4
4	0·697	69·8
5	0·795	73·0
	ACETATE RAYON	
0	0·077	0
1	0·121	25·8
2	0·338	72·3
3	0·467	81·5
4	0·600	89·0
5	—	—

when the average fibre length has attained a certain minimum value the raising machine ceases to be effective as a raising agency, since it merely pulls out fibres from the body of the cloth and deposits them in the flock box.

2. CHANGES IN FABRIC PROPERTIES DURING RAISING

(i) Tensile Strength

It is well known that a cloth which has been excessively raised is weak in the weft direction, but there are few data which show the extent to which this weakening takes place. Determination of the tensile strength of the weft yarns on a large number of fabrics, which had been raised to different extents, yielded results which are given in Tables IV–VI.

Table IV

Fabric Composition	Strength (oz.) of Weft after Raising Stage No.—					
	0	1	2	3	4	5
100% Nylon	115	112	103	60	41	22
100% Bright Fibro ...	62	56	25	24	16	5
100% Matt Fibro ...	57	56	29	14	9	0
100% Rayolanda ...	45	34	31	19	0·4	–
100% Wool	34	34	28	16	0·5	–
100% Acetate rayon	29	27	8	1·0	–	–

Table V
Loss in Strength during Wet Raising*

Man-made Fibre in Weft Yarn (%)	Decrease (%) in Weft Strength after raising for (rounds)—			
	5	10	20	40
FIBROCETA				
21·2	4·8	9·6	20·8	36·0
40·7	9·0	21·8	35·0	43·8
51·0	9·8	23·0	38·4	57·0
59·3	10·6	23·4	43·8	64·7
80·0	12·8	25·2	48·6	70·5
NYLON				
40·8	8·5	20·8	60·2	78·5
50·6	5·7	16·5	53·6	70·2
60·0	4·9	15·3	40·6	67·0
79·7	8·5	10·7	32·2	64·2
VINYON				
20·8	20·8	30·0	49·5	70·5
50·0	15·5	22·2	39·8	62·0
60·0	14·5	20·8	32·5	52·1
80·0	6·7	9·5	25·2	33·7

* The fabrics used in these trials had a cotton warp and wefts made from blends of wool and man-made fibres.

Table VI
Loss in Strength during Dry Raising*

Man-made Fibre in Weft Yarn (%)	Decrease (%) in Weft Strength after raising for (rounds)—					
	10	20	35	50	70	100
FIBROCETA						
21·2	14·4	30·2	35·1	62·0	84·0	—
40·7	16·6	35·4	43·8	66·1	91·0	—
51·0	22·8	42·7	58·5	78·6	—	—
59·3	26·2	43·4	61·8	86·2	—	—
80·0	29·4	60·4	71·6	—	—	—
NYLON						
40·8	16·1	39·2	44·5	50·0	87·6	94·8
50·6	11·5	33·4	38·6	47·0	83·5	91·5
60·0	9·7	32·2	36·1	45·7	80·2	86·2
79·7	6·7	25·4	31·8	43·4	75·2	81·4
VINYON						
20·8	12·6	43·2	61·2	74·2	89·5	—
50·0	21·2	48·8	65·7	78·5	—	—
60·0	24·4	59·7	72·7	89·5	—	—
80·0	32·2	68·5	82·5	—	—	—

* See footnote to Table V

It is evident that in all cases the yarn strength is reduced on raising. The fall in strength and the percentage reduction in strength are, however, dependent on the initial strength of the yarn, and among the fabrics in Table IV the percentage fall is least with the nylon, and greatest with the acetate rayon fabric. Moreover, in the blended cloth, as the proportion of the weaker fibre is increased, so the percentage loss becomes greater. Even with

nylon cloths, however, the fall is appreciable, and the results, as a whole, stress the need for care in raising to avoid making the finished materials weak in the weft direction.

In practice careful choice of weave and yarns is essential, for the cloth must have a sufficiently high initial strength to ensure that the required final effect can be produced without too great a reduction in strength. This is particularly important in the production of styles such as the duvetine. This type of finish, which is becoming increasingly popular, is best obtained by successive raising and cutting, whereby a close, dense, velvety pile is obtained. Unless the cloth is sufficiently strong to withstand the comparatively severe raising conditions, the final effect will be unsatisfactory. The cloth should not be made stronger simply by increasing the twist in the yarn, but two-fold yarn can be used with advantage. The cloth should also be well set.

(ii) Composition of Pile produced from Blended Fabrics

Many man-made fibres are used in blends with natural fibres, and it is important to know whether the composition of the pile produced on raising is the same as or different from that of the cloth from which it has been raised. Experiments carried out on many blended fabrics showed that in certain cases one fibre is raised preferentially. This must, therefore, be taken into account when the fabric is designed. Some of the more important results obtained by raising several blended fabrics, both wet and dry, are shown in Tables VII and VIII.

Table VII
Composition of Pile produced on Blended Fabrics* by Wet Raising
(Man-made fibre, %)

Unraised Weft	Pile	Difference
VINYON		
20·8	17·3	— 3·5
40·2	21·3	—18·9
60·6	35·2	—25·4
80·0	62·9	—17·1
NYLON		
19·8	20·1	+ 0·3
40·8	35·7	— 5·1
60·0	49·1	—10·9
79·7	64·3	—15·4
FIBROCETA		
21·2	19·1	— 2·1
40·7	33·8	— 6·9
59·9	50·3	— 9·6
80·0	74·3	— 5·7
FIBRO		
20·3	26·2	+ 5·9
39·5	40·5	+ 1·0
60·2	62·1	+ 1·9
79·7	79·5	— 0·2
FIBROLANE		
24·9	24·2	— 0·7
49·5	38·0	— 0·5
74·1	74·5	+ 0·4

* See footnote to Table V

TABLE VIII
Composition of Pile produced on Blended Fabrics* by Dry Raising
(Man-made fibre, %)

Unraised Weft	Pile	Difference
	VINYON	
20·8	9·5	−11·3
40·2	16·8	−23·4
60·6	33·7	−26·9
80·0	49·8	−30·2
	NYLON	
19·8	21·3	+ 1·5
40·8	34·9	− 5·9
60·0	50·5	− 9·5
79·7	65·6	−14·1
	FIBROCETA	
21·2	18·0	− 2·2
40·7	22·3	−18·4
59·9	39·9	−20·0
80·0	54·4	−25·6
	FIBRO	
20·3	24·1	+ 3·8
39·5	43·0	+ 3·5
60·2	64·6	+ 4·4
79·7	81·0	+ 1·3
	FIBROLANE	
24·9	22·9	− 2·0
49·5	47·5	− 2·0
74·1	75·6	+ 1·5

* See footnote to Table V

It is evident that in fabrics containing Fibroceta, nylon, and Vinyon the pile obtained after wet or dry raising contains more wool than the weft yarns of the original fabrics. Moreover, as the percentage of the man-made fibre in the original cloth increases, so does the difference between the composition of the pile and that of the weft in the unraised cloth. The proportion of wool and Fibro, or of wool and Fibrolane, in the pile obtained on a blended cloth containing the two fibres is approximately the same as that in the unraised cloth.

It should be stressed that the structure of the fabrics greatly affects the magnitude and the changes in pile composition, and the results given above should be regarded only as indicating general trends. There is no doubt, however, that fibres are preferentially raised.

3. CHANGES IN DIMENSIONS

The changes in dimensions of textile fabrics during raising are in general comparatively small, but there is a tendency for the fabric to be pulled lengthways and to contract in width. With some of the longer and stronger fibres, however, considerable contraction in width may occur, which can be undesirable. It arises presumably from an increase in weft crimp during raising, and seems to be associated particularly with strong weft yarns made from strong fibres. The phenomenon is illustrated by the fibres given in Table IX. Although undesirable in many cases, some of these raised fabrics are very attractive, for they have a dense, fluffy surface which resembles that obtained on a milled woollen. The phenomenon occurs

with staple nylon fabrics made in a wide range of structures.

TABLE IX
Shrinkage of Cotton-warp Fabrics during Raising

Weft	Strength of Weft (lb.)	Shrinkage during Raising (%)
Rayolanda	10·2	8·4
Fibro	9·1	8·5
Fibro	11·2	8·7
Cotton	2·0	1·6
Cotton	13·2	1·5
Tenasco	15·8	11·0
Fortisan	16·3	19·4
Nylon waste (silk-spun) ...	11·1	23·7
Nylon waste (woollen-spun)...	12·2	9·1

Factors influencing Raising

1. RAW MATERIAL

Fabrics made from almost any textile fibre can be raised, but the type of pile obtained varies widely according to the raw material. It is generally accepted, for example, that the coarser fibres of long staple are particularly suited for the production of rugs and blankets, whereas finer materials are best suited for the production of fabrics in which a short, dense pile is required. Density and length of pile seem to be governed by fibre fineness and length respectively. The various synthetic fibres differ in their susceptibility to raising. Fibro and nylon fabrics are generally less susceptible to raising than corresponding wool fabrics, while those containing protein rayons or Rayolanda are more easily raised. The magnitude of these differences is, however, dependent on the structure of the fabric. But it should be stressed that, by suitable control of raising conditions, excellent effects can be obtained on almost any type of fabric. It would not be expected, for example, that similar effects could be obtained by raising a rayon cloth under the same conditions as a comparable cotton or wool fabric.

2. CLOTH STRUCTURE

The susceptibility of a fabric to raising is greatly affected by the structure of the yarns and of the cloth, as indicated by the results given in Tables

TABLE X

Structure of Fabric		Increase in Thickness on Raising (%)
Weave	Picks/in.	
Plain	24	0·3
2/2 Hopsack	30	35
4/4 Hopsack	46	100
2/2 Warp rib	34	25
4/4 Warp rib	46	47
2/2 Weft rib	34	70
4/4 Weft rib	38	83
1/3 Twill	32	15
3/5 Twill	42	46
4/4 Twill	32	42
2/2 Twill	32	32
Twilled hopsack	32	63
8-end sateen	47	78

TABLE XI

Type of Weave	Increase in Thickness on Raising (mm.)
Plain	0·99
2/2 Matt	2·05
3/3 Matt	3·17
6/6 Matt	3·95
2/2 Twill	1·97
1/3 Twill	2·91
1/5 Twill	3·79
2/4 Twill	3·37
3/3 Twill	3·03
1/11 Twill	4·60
2/10 Twill	4·27
3/9 Twill	3·83
4/8 Twill	4·19
5/7 Twill	4·4
6/6 Twill	4·81
4-end sateen	3·51
6-end sateen	4·93
12-end sateen	5·82

X and XI, which summarise the increase in thickness following raising of cloths of various structures. It is evident that the plain-weave fabric is the most difficult to raise, and cloths with long weft floats yielded the most pile. Moreover, in all cases the greater the number of picks (the number of ends remaining constant), the more difficult is the cloth to raise, although the change produced by increasing the set by a given amount varies with the type of weave. Increasing the amount of twist in the yarn makes the cloth more difficult to raise.

TABLE XII

Twist in Weft Yarn (t.p.in.)	Wt. of Pile (g.)
4	0·18
12	0·10
18	0·08

This is illustrated by the figures given in Table XII, which refers to the results obtained by raising cloths of identical structure but made from weft yarns of different twists.

3. RAISING CONDITIONS

(i) Moisture

In general, wet cloths yield more pile than dry cloths, unless raising is carried out for an excessively long time. This is illustrated by the figures given in Table XIII. There are, however, exceptions to this rule, for if the cloth is very heavily set it may become boardy. This happens frequently with Fibro fabrics, for the wetted cloth is densely packed; moreover, as the wet strength of fibres is low, a considerable amount of fibre is torn off and finds its way either into the flock box or in the raising agency. The difference in wet and dry raising is small with fibres such as Terylene and nylon. As indicated earlier, the presence of

TABLE XIII
Comparison of Wet and Dry Raising

Material	Wt. of Pile after Raising (g.)	
	Dry	Wet
Wool	0·14	0·20
Wool	0·22	0·27
Fibro	0·36	0·21
Rayolanda	0·54	0·36

moisture affects the composition of the pile produced. This observation emphasises the need to maintain the moisture content of a fabric constant during raising, for otherwise uneven results can be obtained. This is particularly marked in cloths made from staple rayon, both cellulosic and protein. When raising fabrics containing rayon, an excessive moisture content should be avoided, but very interesting effects can be obtained on fabrics which are uniformly damp.

(ii) Acids and Alkalis

It has been found that wool cloths that are acid or alkaline are raised more readily than those which are neutral. The results obtained by raising damp cloths which have been immersed in various buffer solutions and centrifuged, and by raising cloths which have been immersed in acid solutions, centrifuged and dried, and then raised, are given in Tables XIV and XV. The general resemblance between these results and the effect of pH on the work required to stretch fibres in various media[3] suggests that the elastic properties of fibres are of importance in determining the resistance to raising.

Since a decrease in the work necessary to stretch fibres facilitates raising, weak acids should be more effective than strong acids at the same pH values.

TABLE XIV
Wet Raising of 100% Wool Cloth

pH	Wt. of Pile (g.)
0·5	0·270
1·4	0·225
2·9	0·185
5·2	0·130
7·3	0·115
9·2	0·125
11·0	0·150
12·1	0·170

TABLE XV
Dry Raising of 100% Wool Cloth

Treatment of Cloth	Thickness of Cloth after Raising (cm.)
Untreated	0·46
1% Hydrochloric acid	0·56
2% Acetic acid	0·64
4% Acetic acid	0·68
6% Acetic acid	0·66
8% Acetic acid	0·71
2% Borax	0·53

TABLE XVI

Treatment of Wool Cloth		Wt. of Pile (g.)
Sulphuric acid (pH 1·96)	...	0·135
Acetic acid (pH 1·96)...	...	0·165

This is, in fact, so, as shown by the results given in Table XVI, which summarises data obtained by wet-raising fabrics of the same pH values but in presence of reagents of different swelling powers. It is interesting that the presence of acids and swelling agents also facilitates raising of Fibro fabrics, but not to the same extent. By raising a

Fibro cloth in presence of water, the weight of pile obtained was 0·10 g.; while in presence of 0·1 N. acetic acid the amount of pile was 0·12 g. Treatment of fabrics containing acetate rayon with swelling agents can produce interesting effects of another type [4]. If the concentrations of the swelling agents are sufficiently high, the fibres become glued together or so weak as to be useless for pile formation. Pile is, therefore, difficult to raise from the body of the cloth, and raising is slow and difficult. Phenol and formic acid can be used for this purpose.

(iii) Neutral Salts

If swelling agents facilitate raising, then it would be expected that reagents which depress swelling would hinder raising. This might account for the fact that solutions of neutral salts tend to hinder pile production, as illustrated by the figures given in Table XVII.

TABLE XVII
Effects of Salts on Raising

Reagent	Increase in Thickness* after raising for—	
	12 rounds	24 rounds
NaCl soln.		
1%	181	550
3%	226	533
5%	174	449
10%	91	347
Saturated	94	346
NaCl in 1% Teepol (Shell) soln.		
1%	301	456
3%	300	497
5%	283	396
10%	271	356
$NH_4H_2PO_4$ soln.		
1%	354	692
3%	300	541
5%	233	314
10%	110	240
Saturated	126	217
Na tungstate soln.		
1%	244	352
3%	202	393
5%	204	286
10%	182	254
Saturated	115	155

* Arbitrary units

This result is of importance in view of the increasing interest in raising proofed cellulosic textiles. The adverse effects are no doubt due to several factors. Swelling may be one, but there is no doubt that the increased friction between the fibres is also important.

(iv) Bleaching

The effect of this process on raising has been studied mainly in respect of wool cloths [5]. Sulphur stoving was originally the only way in which blankets could be bleached, but the objectionable smell of the stoved cloth and the tendency of the fabric to become yellow on exposure to light has caused many blanket manufacturers to substitute hydrogen peroxide bleaching for sulphur stoving. The ease of raising of the cloth bleached with peroxide is, however, less than that of the stoved product, especially if the alkaline peroxide process is used (see Table XVIII).

TABLE XVIII

Treatment of Fabric	Thickness after Raising (cm.)
None	0·59
Bleached in 2-vol. H_2O_2 (alkaline) for 17 hr. at 18°c.	0·60
Bleached by impregnating with 10-vol. H_2O_2 (alkaline) and ageing	0·63
Bleached by immersing in 2-vol. H_2O_2 (alkaline) for 17 hr. at 18°c. followed by stoving	0·75
Double stoving	0·77

The susceptibility to raising of the bleached blankets is increased by rinsing them in acid before they are raised, or by using an acid peroxide process.

(v) Dyeing

The pH value also appears to be important when considering the effect of dyes on the susceptibility of the fabric to raising. This is evident from the results given in Table XIX. While recognising the considerable variations among individual dyes in each group [6], it is significant that, with the exception of the mordant dyes, the lower the

TABLE XIX

Class of Dyes	Average pH of Residual Dyebath	Average Raising Effectiveness	
		Dry	Wet
Undyed cloth	—	143	216
Metal-complex	2·33	173	216
Levelling acid	2·56	146	208
Acid milling	5·30	112	175
Neutral-dyeing acid	7·28	94	166
Direct cotton	8·00	60	162
Mordant—			
(a) Afterchrome	4·21	97	166
(b) On mordanted material	5·09	89	154
Indigo	9·8–9·9	109	157

final pH of the dyebath, the more easily is the dyed fabric raised. This observation has become important in relation to the raising of wool–Fibro mixtures. If only the wool in the blended cloth is dyed, the dyed fabric raises easily; but if both components are coloured by dyeing the Fibro separately or by using dyes which dye both fibres in the same bath, the raised dyed cloth is thin and poor, and pile production is not good. Better results are obtained if it is not necessary to dye the cellulosic component, e.g. when spun-coloured Fibro is used as a component of the blend to avoid the need for filling in the Fibro. Alternatively, the susceptibility of the cloth to raising can be improved by an aftertreatment with an acid or a lubricant.

(vi) Lubricants

Since in raising fibres are lifted out from the body of the cloth, it would be expected that the presence of lubricants would facilitate the process. This has been found to be so, and the figures given

in Tables XX and XXI indicate that both dry and wet raising are facilitated by the presence of lubricants such as soap, Teepol, or Lubrol W (ICI). The effect is marked with a wide range of fabrics made from wool, Fibro, or Tenasco, and Table XXI shows clearly that fabrics of different susceptibilities to raising are improved by the presence of lubricants. In view of these results it would be expected that anti-lubricants would hinder raising, and the values given in Table XXII confirm this.

TABLE XX
Wet Raising in presence of Lubricants

Medium	Wt. of Pile (g.)
WOOL CLOTH	
Water	0·150
1% Teepol	0·165
5% Teepol	0·268
2·5% Soap	0·360
FIBRO CLOTH	
Water	0·190
1% Teepol	0·240
2·5% Soap	0·290

TABLE XXI
Raising of Tenasco Fabric

Fabric	Increase in Thickness* on raising in—	
	Absence of Lubricant	Presence of Lubricant
I	107	112
II	108	119
III	108	139
IV	115	120
V	105	125
VI	83	114
VII	23	62

* Arbitrary units

TABLE XXII

Fabric	Thickness of Raised Material (cm.)
Untreated	0·44
Treated with 1% Syton* and raised dry...	0·34
Treated with 1% Syton* and raised wet...	0·39

* Monsanto

Conclusion

The data summarised in the previous pages emphasise the complexity of the raising process. Of particular importance is the large number of factors which affect the results. This necessitates careful control if the best results are to be obtained, but it also points the way to obtaining new and novel effects by raising. If the amount of pile produced by a given mechanical treatment is so easily affected, then it is clearly possible to obtain many interesting styles by printing with reagents which increase or decrease pile production, and then raising. Again, purely mechanical devices can be used for "gluing" the fibres together, and so preventing their being lifted from the cloth. In this category comes the use of hot embossing calenders and steaming treatments before raising as a means of obtaining novel effects. Researches such as those described in the present paper are merely of a preliminary nature, but the results have served to demonstrate quite clearly that raising should not be considered simply as the scratching of fibres to the surface of a cloth. It is much more than that. It is a cloth-finishing process capable of rationalisation and refinement. When regarded in this way, taking advantage of the many new finishing agents which are being developed in the light of the many new chemical techniques now available, cloth raising offers great scope, not only for development engineers to design new and more readily controlled raising machines, but also for the chemical technologist to develop new reagents which will facilitate the production of new styles Co-operation between the chemically minded finisher and the cloth designer will ensure that raising will be a valuable tool in providing the public with decorative and useful textiles.

*   *   *

The data given in Table XXI were obtained in collaboration with Mr. T. G. Allen of the Dyeing Department of Messrs. Courtaulds Ltd., Coventry, during the course of a larger investigation. The author wishes to acknowledge the help given by Mr. Allen in this work.

Many of the fabrics used in this investigation were supplied by the Use–Development Organisation of Messrs. Courtaulds Ltd.

DEPARTMENT OF TEXTILE INDUSTRIES
    UNIVERSITY OF LEEDS

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Discussion

Mr. H. W. BEST-GORDON: Has the lecturer studied the effect on fibre breakage of yarn twist direction; e.g. does a fabric constructed with warp and weft in similar direction of twist behave differently from one in which opposing twist directions are used?

Prof. WHEWELL: We have carried out only a limited number of trials to determine the fibre

breakage during raising, and the work has not yet been extended to find the effect of fabric construction on fibre breakage.

Mr. BEST-GORDON: Could the lecturer give some indication of the surface helix angle in relation to the yarn axis of the examples given in Table XII, because the yarn count is not stated? Has this factor been considered in the assessment of the degree of raising? It appears to me that a definition of this type would be more applicable than reference to twist in turns per inch.

Prof. WHEWELL: The yarns used in the trials reported in Table XII were 1/12s worsted counts. Since all had the same count, the tangent of the helix angle is directly proportional to the number of turns per inch. Further work is in progress on this topic.

Mr. G. H. HEAP: I think that Professor Whewell has overemphasised the need for fibre breakage. Some must take place, but this should be kept to a minimum. The cover is mainly produced by drawing out fibre ends. Therefore, the twist factor of the yarn deserves more attention, as this is frequently too high to give satisfactory raising. Similarly, if much raise is required, staple length cannot be too long, or fibre breakage will increase. The limiting case is continuous filament, where all raising must be by fibre breakage. Experience shows that the raising of Terylene continuous-filament industrial cloth, is entirely haphazard, and much better results can be obtained by using staple fibre.

Prof. WHEWELL: It is agreed that fibre breakage is not solely responsible for pile production in all cases, and that by careful choice of twist the possibility of drawing out fibres can be greatly enhanced. Work is in progress which will enable the extent of fibre breakage to be assessed on a wide range of materials. There is no doubt, however, that in many cloths made for the wool trade there is significant fibre breakage, and that cloths have to be designed to take this into account. It is difficult to conceive how, for example, a fibre which is 4 in. long can be lifted out of a yarn to form a pile without being broken.

Mr. J. RAYMENT: With respect to Mr. Heap's comments regarding the mechanism of brushing being the raising of the fibre ends and not fibre breakage, I would like to suggest that the increase in ease of brushing resulting from fibre lubrication is due to a release of interfibre cohesion allowing the points of the carding to pluck up the fibres sufficiently to allow them to be broken. The lubrication effected in these tests would not be sufficient to allow the ends of the fibres to be disentangled without breakage.

Dr. N. LANDQVIST: Since the fibre friction seems to be of importance for the raising properties, have any fibre friction measurements been carried out in connection with studies of raising? It might be suggested that the turn–elongation curve obtained when untwisting a yarn under a constant load can be of some interest in this case.

Prof. WHEWELL: Some measurements have been made, and in general the lower the coefficient of friction of the fibres in the yarn the more easily are the fibres lifted out of the cloth.

Mr. RAYMENT: The use of acetic acid as a brushing assistant seems to be very promising. I would be pleased to know what were the conditions of application and the maximum drying temperature used.

On the subject of moisture content, I have noticed that, when trying new auxiliaries for both viscose and acetate rayon fabrics, better results have been frequently obtained when the fabric has been taken straight from the stenter than when allowed to condition thoroughly. Whilst the accumulation of static charge might be suggested, I scarcely think that this accounts for the observation, since many of the auxiliaries tried have also been used as antistatic finishes.

Prof. WHEWELL: The fabric was simply soaked in the acid and dried at room temperature.

Mr. R. J. S. LINN: We experience different raised effects with different dyes applied to viscose and acetate rayon warp-knitted fabrics. Could Prof. Whewell enlarge on this at the present stage of his investigations?

Prof. WHEWELL: There is no doubt that the process of dyeing affects the ease with which fibres are lifted out of the cloth. This is probably connected with modifications in either the elastic properties or the surface friction of the fibres. In the experiments which have been carried out so far, it has not been possible to prove that fabrics dyed different *colours* raise differently, although there is no doubt that in the trade it is believed that the particular colour of a cloth is intimately connected with the response to raising.

Mr. LINN: When continuous-filament rayon (warp-)knitted fabric is raised, I do not know where the pile comes from if not from fibre breakage.

Prof. WHEWELL: There is no doubt that when continuous-filament fabrics are raised the pile comes from fibre breakage.

Mr. E. MOSS[*]: In our experience at the Shirley Institute, warpway extension of cloths on raising depends on the conditions of raising and the setting of the machine. In general, we have found that there is little change in warpway dimension during the raising of cotton flannelettes. We have found also that, with cotton, the loss in strength weftways is proportional to the amount of pile over the middle range, but there is evidence that at first— say up to the second run— raising takes place with little or no loss in strength. This might be taken as evidence that little fibre breakage occurs, at least in the early stages. As far as cloth construction is concerned, flannelettes have long been constructed to be approximately twice as strong weftways as warpways before raising, so that after raising to a commonly accepted 50% loss of strength they become about square in strength.

* Communicated

The High-temperature Dyeing of Cellulosic Fibres

ANDREAS SCHMITZ*

The fundamental principles determining the effect of elevated temperature on the substantivity, the rate of dyeing, and the levelling power of direct dyes are discussed with the aid of exhaustion curves. Since less dye is absorbed above 100°c. than at normal dyeing temperatures, dyeing should be continued in a cooling dyebath after the high-temperature stage. Although the equilibrium concentration of dye on the fibre is attained more rapidly at higher temperatures, the amount of dye absorbed in unit time is lower, provided that the dye liquor has free access to the fibre. Reasons for the more rapid dyeing observed in practice are better levelling power and reduced swelling: at lower temperatures swelling tends to constrict the interstices between the individual fibres, through which liquor can flow. An explanation is given for the surprising fact that the increase in levelling power produced by a given rise in temperature does not depend on its value at the lower temperature. Vat dyes and synthetic fibres are considered briefly.

Dyeing at high temperatures has been attracting steadily growing interest, especially during the past few years, as shown by the large number of papers, from many different countries. My aim in this paper is not to summarise this work, but rather to seek out fundamental principles, and on their basis to explain and correlate the experimental results, especially those obtained in our own laboratories.

The British school in particular has shown how to apply the laws of classical physical chemistry to the processes involved in textile finishing, and has thus obtained very interesting and informative results. Although from the nature of this work it has been carried out with highly purified dyes and materials, it has provided us with a tool for the successful study of practical dyeing processes.

In the pattern cards of many dyemakers the dyeing properties and behaviour of the dyes are accurately represented by means of graphs or tables. These data have been determined on commercial dyes in the types of dye liquors encountered in practice. They are a valuable aid to the practical dyer, and could be to an even greater extent if their significance were appreciated everywhere. For this reason I, too, have attempted to explain the processes involved in high-temperature dyeing on the basis of these values and their extension beyond 100°c. The fact that in many cases only approximate equations have been employed is admittedly not altogether justifiable from the mathematical point of view, but nevertheless is of assistance in allowing the nature of the processes concerned to be recognised all the more clearly.

The chief cellulosic fibres of interest in high-temperature dyeing are cotton and viscose and cuprammonium rayon filament and staple. Owing to differences in fine structure, these fibres show wide differences in behaviour under normal dyeing conditions, and corresponding differences can be observed in high-temperature dyeing, although to a much smaller extent. In spite of these differences, the laws governing high-temperature dyeing may be derived in a completely analogous manner for all the fibres mentioned. Because of this it is better not to group our observations according to the types of fibre but rather to discuss the classes of dyes separately, since very considerable and obvious differences occur in this respect.

1. DIRECT COTTON DYES

Apart from a few exceptions, dyes of this class are represented by the disazo and polyazo dyes. This fact is of decisive importance in connection with the stability of the dyes at temperatures above 100°c.

From experience of the normal dyeing process it is known that a few direct dyes show a tendency towards reduction on boiling under unfavourable conditions and with lengthy dyeing times; i.e. the dyeings become more and more dull and flat as time progresses, and in particularly bad instances a complete change of hue has actually been known to occur. However, this phenomenon can nearly always be avoided by adding special protective agents.

In this respect, conditions in the high-temperature process are particularly unfavourable, and it would appear to be appropriate to examine the nature of this phenomenon more closely. This is quite obviously a case of reduction phenomena which are caused by impurities in the goods being dyed or by degradation products of the fibre material, and which are assisted by elevated temperatures and alkalinity of the dyebath.

The resistance of different dyes to these influences varies considerably, and examination of the constitution of a large number of dyes has shown that exposed azo groups are those chiefly attacked by the reducing substances, whereas azo groups protected by other substituent groups are not split up—

Readily reducible   Difficulty reducible
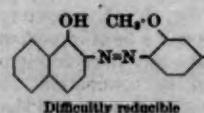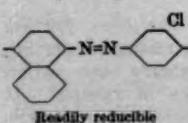
*In the absence of Dr. Schmitz, the paper was presented by Dr. F. Gund.

Here it is possible to observe a very distinct relationship to the dischargeability of direct dyes, only a few dyes not showing this relation. Although reduction processes are involved in each case, it is not possible to draw a complete parallel in view of the different conditions (cf. Table I).

TABLE I

Sirius Supra Dye	Tendency towards Degradation by Boiling	Alkaline Dischargeability
Yellow RT	Very slight	Not dischargeable
Orange RRL	Very slight	Bad
Blue FBGL	Very slight	Moderate
Red 4BL	Fairly marked	Very good
Green BB	Very strong	Very good

To prevent degradation of the dyes during high-temperature dyeing it is thus important to avoid a reducing environment. This can be achieved by ensuring particularly careful preliminary cleansing of the goods to be dyed in order to remove completely any size or other preparations from the fibre and also, in the case of cotton, the natural non-cellulosic impurities.

In addition, the pH of the dyebath must be kept as low as possible. For this reason it is inadvisable to add soda or alkaline phosphates to the liquor, as is often still the practice, and care should be taken to see that no alkali is introduced with the goods from pretreatment baths. Attention should also be paid to the water employed, especially as this is often softened, and may contain quite large amounts of sodium carbonate and sodium bicarbonate.

There has been no lack of attempts to remedy these conditions by making special additions to the dyebath. For example, it has been suggested that *m*-nitrobenzenesulphonic acid, which is a familiar product in textile printing, should be used as a weak oxidising agent. However, a trial in our laboratories revealed no special protective effect. On the other hand, a mixture of sodium chromate and ammonium sulphate, which is marketed as "Monochrome Mordant"[1], proved very effective. Only in the case of a few dyes which are sensitive to metals was there a slight dulling, apparently owing to the partial formation of a chromium lake. This can be avoided, however, if a mixture of potassium chlorate and ammonium acetate, which has a quite similar effect, is used as a protective agent. The former salt acts as an oxidising agent and the latter as a buffer to remove any alkali which may be present.

The Farbenfabriken Bayer AG. have carefully examined the behaviour of the majority of their direct dyes (Benzamine, Benzo, Benzo Viscose, Benzo Fast Copper, and Sirius ranges) under high-temperature dyeing conditions, and the results of these tests have already been published by E. Herrmann[1,2]. A report on the corresponding trials conducted with ICI dyes was published by K. Butterworth[3]. From these results it is quite apparent that a large number of dyes are available for dyeing at temperatures above 100°C., and

that it is possible to achieve good results with them if the above conditions are taken into consideration.

Having considered the chemical requirements for high-temperature dyeing, let us turn our attention to the physicochemical principles on the basis of which we can obtain further information on substantivity, rate of dyeing, and levelling power at elevated temperatures.

Nowadays many dyemakers include values for the exhaustion of the dyebath at various temperatures in their pattern cards and circulars. For practical reasons these readings are made after a dyeing time of 60 min. Thus the graphs show the effect of temperature on the percentage of the initial amount of dye deposited upon the fibre at the end of one hour. Two typical curves are shown in Fig. 1.

(i) 2% Sirius Yellow GC on viscose rayon
(ii) Sirius Orange G on viscose rayon
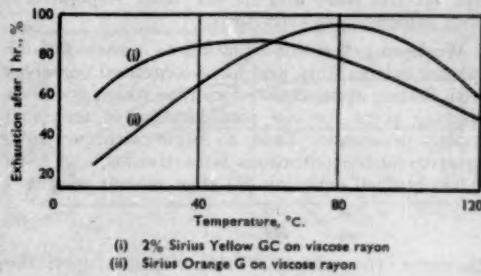
FIG. 1

These curves have proved to be very useful in practical dyeing, and have provided much information on the behaviour of the dyes and their compatibility. However, they do not show the maximum absorption by the fibre at the various temperatures, since, especially at lower temperatures, there is insufficient time for thermodynamic equilibrium to be reached. This is shown diagrammatically in Fig. 2, which gives typical exhaustion–temperature curves for a single dye after various times of dyeing.

Time of Dyeing
(i) ∞
(ii) 60 min.
(iii) 15 min.
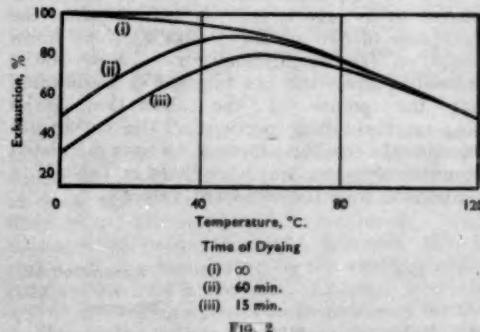
FIG. 2

From Fig. 2 it is clear that the curves, especially at the lower temperatures, approach a limiting curve as the time is increased, and this shows the maximum amounts of dye which the fibre can absorb at the various temperatures. Thus, this

limiting curve gives the thermodynamic equilibrium absorptions for the various temperatures as determined by the true physicochemical affinity.

This equilibrium curve is of special importance in high-temperature dyeing, since the high rate of diffusion at elevated temperatures results in these equilibrium concentrations being attained practically within normal dyeing times.

The calculation of the affinity as the change in entropy of the dye–fibre system during the dyeing process has already been carried out by the British workers Vickerstaff[4] and Marshall and Peters[5] by the method of Gibbs. The equation derived by them is as follows—

$$-\Delta G = RT \ln \frac{a_f}{a_s} \qquad \text{(i)}$$

$(-\Delta G =$ affinity; $R =$ general gas constant; $T =$ absolute temperature; a_f and $a_s =$ amounts of dye on the fibre and in the bath respectively, both calculated as activities).

We have taken this equation as a basis for our further calculations, and have contented ourselves with finding approximate formulae which give us a starting point for our consideration of technical dyeing processes. Thus, to begin with, we have substituted concentrations for activities, and have thus obtained equation (ii) after rearrangement—

$$\ln \frac{c_f}{c_s} = -\frac{\Delta G}{RT} \qquad \text{(ii)}$$

However, the affinity, $-\Delta G$, depends upon the temperature, and may be replaced by the approximate formula[6]—

$$-\Delta G = -\Delta G_0 + \text{const} \times (T_0 - T) \qquad \text{(iii)}$$

If equation (iii) is substituted in equation (ii), and simplified by combining the constants, equation (iv) is obtained in which X and Y are constants which are characteristic of each dye—

$$\ln \frac{c_f}{c_s} = \frac{X}{T} + Y \qquad \text{(iv)}$$

We can now use equation (iv) to calculate any points on the equilibrium curve, provided that we know two such points to work out the constants X and Y. In addition, a point of particular interest to us here is that we can calculate the absorption of dye at 120°c. (248°F.) if we know points on the equilibrium curve below 100°c. Proceeding upon the not unjustified assumption that the points of the absorption graph lying on the falling portion of the curve also belong to the equilibrium curve, we have calculated a number of values, which are listed in Table II in comparison with the measured values.

TABLE II

Dye	X	Y	Exhaustion at 120°c. (%)	
			Measured	Calc.
Sirius Yellow GC	−2185	−4·45	42	39
Benzo Yellow L	−3410	−7·36	48	50
Sirius Red BB	−2210	−4·57	37	36

The most important information given by these curves and data is that the cellulose fibre always absorbs less dye at temperatures above 100°c.

than at normal dyeing temperatures, regardless of the dye and the dyeing time involved. This difference varies in extent with individual dyes, but is quite appreciable in every case.

This fact is of special importance. On the one hand it can be used for assessing the levelling power of the dyes, as we shall discuss later. On the other hand this "lower yield" is of considerable economic importance. Even if it were technically possible, this factor alone would prevent one from ever breaking off dyeing at an elevated temperature, since a large proportion of the dye would be drained off without being used. Because of this, the dyebath should be allowed to cool off again after the high-temperature stage, especially where full colours are concerned, in order to allow the remaining dye to be absorbed.

If this process is carried out very slowly, the dye absorption will change along the equilibrium curve. However, as there is not usually sufficient time available for this, the curve representing absorption of dye at falling temperatures lies somewhat below (Fig. 3).

(i)   Rising temperature
(ii) Equilibrium curve
(iii) Falling temperature
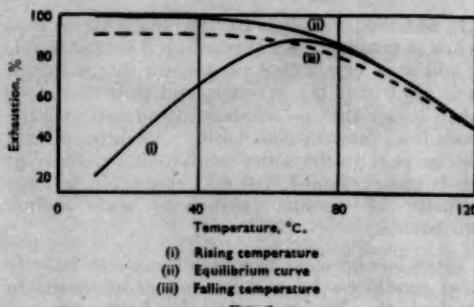
Fig. 3

This absorption process thus results in a greater colour yield upon the fibre than would be the case if dyeing were discontinued at 120°c. However, it also gives rise to a few problems, since it is difficult to control. This applies particularly to mixture dyeings, especially when these are used for delicate mode shades. For this reason it is a good plan, in the case of standard shades which frequently recur, to draw up a precise schedule for temperature sequences and dyeing times, so that it is possible to dye "blind to pattern". Another method is possible and is used in the trade. Dyeing is conducted at elevated temperatures for only a short period, and then the batch is allowed to run further at temperatures below 100°c., so that dyeing can always be discontinued immediately after the required shade has been attained. This process makes use of the advantages of high-temperature dyeing, such as good penetration of the dye, reduction in swelling of the mass of material, and easier levelling, whilst still avoiding the disadvantages discussed above.

Although the equilibrium distribution of a dye between fibre and dyebath and its dependence on temperature are thus of great importance in high-temperature as well as normal dyeing, it is

also important to know the time taken to reach this state of equilibrium or any other state. The dependence of the rate of dyeing of a dye upon temperature and its relationship to the equilibrium state are extremely interesting and specially important at high temperatures, and will therefore be considered in greater detail.

It may be assumed that, at the start of dyeing, only the outer surface of the goods, i.e. the surface of the individual fibres, is in contact with the dye liquor. At the fibre surface the state of equilibrium, which is determined solely by the temperature, will thus be established immediately. Dye then diffuses from the surface towards the centre of the fibre, whilst the dye liquor continues depositing fresh dye molecules on the surface of the fibre, so that the equilibrium concentration is always maintained there.

Diffusion is the slowest stage in this sequence, and thus determines the speed of the whole process. It is governed by Fick's law—

$$\frac{dn}{dt} = DA \frac{dc}{dl} \qquad (v)$$

which states that the amount of dye diffusing in unit time is proportional to the diffusion coefficient D, the area A perpendicular to the direction of diffusion, and the concentration gradient.

This differential equation can be integrated only with the aid of certain limiting conditions. Incidentally its exact mathematical treatment has been undertaken by Hill [7] for another application. This produces the following equation, which is, however, very difficult to work with—

$$c_{ft} = c_{f\infty}\left[1 - 4\left(\frac{\exp(-5\cdot75\ Dt/r^2)}{5\cdot75} \right.\right.$$
$$\left.\left. + \frac{(\exp(-30\cdot2\ Dt/r^2)}{30\cdot2} + \ldots \right) \right] \qquad (vi)$$

where c_{ft} and $c_{f\infty}$ represent the concentration of dye on the fibre at times t and ∞ (equilibrium concentration) respectively, and r is the radius of the fibre. Boulton [8, 9] also examined the validity of this equation experimentally. It can be applied exactly only provided that the concentration of dye in the bath does not decrease during dyeing and the liquor flows freely over the fibre*. Such conditions are seldom achieved in practice.

However, since we are concerned here mainly with fundamental principles, we need not hesitate to make use of this equation for cases occurring in practice. We can even neglect the higher c terms, which are really only correction terms, and then arrive at the following simple, approximate equation—

$$c_{ft} = c_{f\infty}\ [1 - 0\cdot7\ \exp(-Dt.\text{const})] \qquad (vii)$$

As we know from comparison with corresponding experimental values, this equation gives a good approximation to the conditions. The concentration c_{ft}, which should be regarded as a mean value over the whole cross-section of the fibre, is thus

* The question of a finite or an infinite dyebath is regarded by Crank [5] in a different manner, but this is not of great importance for our problem.

determined by two quantities, each of which depends in a different way upon the temperature.

Rise in temperature produces the following effects—

(1) The equilibrium concentration $c_{f\infty}$ at first falls only very slightly, but with further rise in temperature it becomes smaller at an ever increasing rate.

(2) The factor $[1 - 0\cdot7\exp(-Dt.\text{const})]$ increases slowly and steadily.

At lower temperatures the influence of the second factor is preponderant, and the amount of dye absorbed after a certain time first increases as the temperature rises. On the other hand, at higher temperatures the influence of the first factor becomes stronger and stronger, so that the rate of absorption falls after a certain temperature is passed (Fig. 4).
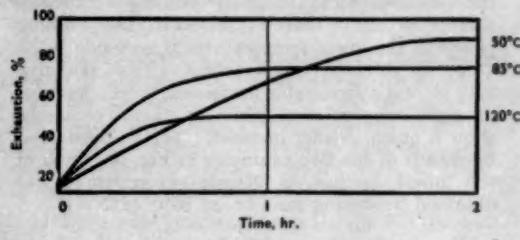

FIG. 4

As far as high-temperature dyeing is concerned, therefore, we can draw the conclusion that, although the equilibrium concentration is attained more rapidly on the fibre, the actual rate of absorption, i.e. the amount of dye absorbed in unit time, is in every case *lower* than at the normal dyeing temperatures of 80-90°C. (176-194°F.). At first glance this fact seems to be completely opposed to practical experience. However, it was possible to confirm this by measurements made in our laboratory.

One of the reasons why reduction in dyeing time occurs in practice is the better levelling possessed by dyes at elevated temperatures, which means that the whole working process can be performed more quickly. This will be considered later.

Another and rather extraordinary reason is the behaviour of the fibre itself. As already stated, equations (vi) and (vii) are applicable only in cases where the flow of dye liquor around the fibre is uninterrupted and unhampered. With packages or packed material, however, this is really not the case, owing to the swelling which constantly occurs in the fibre. Although a certain degree of swelling appears to be necessary for the dyeing process, if this is too great the effect is to constrict the interstices between the individual fibres to such an extent that adequate circulation of the liquor becomes impossible. It is well known that swelling of the fibre decreases with a rise in temperature, and this is apparently specially

marked at temperatures above 100°c. The fact that this decrease in swelling is most pronounced in regenerated celluloses is a reason for the special importance of the high-temperature process for this type of fibre.

A characteristic feature of high-temperature dyeing is the often considerable increase in the levelling of dyes, i.e. the migration of dye from places of higher concentration to other places on the goods which have absorbed less dye.

Levelling power is often assessed in the laboratory by placing a dyed skein together with an undyed skein in the old dyebath or perhaps in a blank bath not containing dye. A note is then made of the time taken to produce complete levelling between the two skeins, i.e. until they possess the same depth of colour.

In our laboratory E. Herrmann has recently made the interesting observation that, although the time required for complete levelling is generally shorter at 120°c. than e.g. at 85°c., the levelling power at the lower temperatures is no guide to its value at elevated temperatures. Thus one dye may show a considerable increase in levelling power at high temperatures, while another dye might show a much smaller increase. This is illustrated by means of the two examples in Fig. 5. Each of the initial dyeings on viscose rayon staple was obtained by dyeing for 1 hr. at 85°c. (185°F.).

(i) Sirius Supra Blue BRR
(ii) Sirius Supra Red 5B
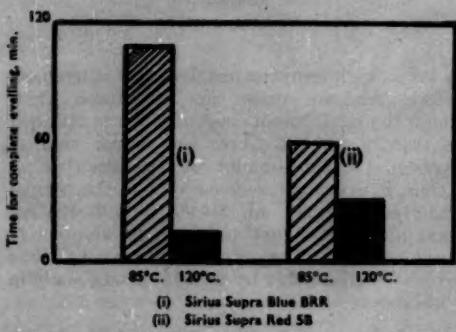
FIG. 5

In order to explain this behaviour we must bear in mind the fact that the levelling process consists of two steps. The first is desorption, i.e. migration of dye from dyed material into the bath. At the same time, however, this dye begins to be absorbed by the undyed material. These stages may be studied by means of dyeing curves similar to those contained in pattern cards.

If the levelling test is carried out at the same temperature (85°c.) as the original dyeings, we can roughly say that the rates of desorption of the two dyes correspond to their rates of absorption. Since there is no change in the state of equilibrium because the temperature remains unchanged, there should actually be no cause for the dyes to migrate from the dyed fibre. This occurs only because the equilibrium is continually disturbed by the undyed material, which absorbs dye already present in the bath. In other words, levelling is

(i) Sirius Supra Blue BRR
(ii) Sirius Supra Red 5B
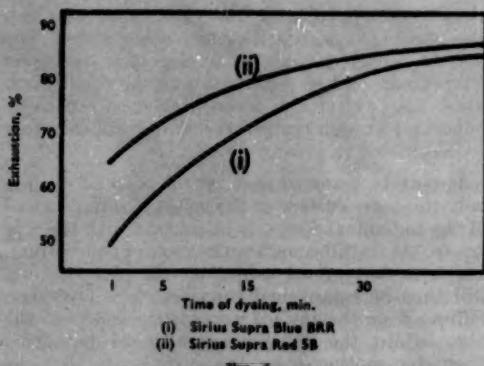
FIG. 6

governed solely by the rate of absorption into the undyed fibre. We can see from Fig. 6, however, that Sirius Supra Blue BRR is absorbed distinctly more slowly than Sirius Supra Red 5B, and thus levelling is slower than with the latter.

(i) Sirius Supra Blue BRR
(ii) Sirius Supra Red 5B
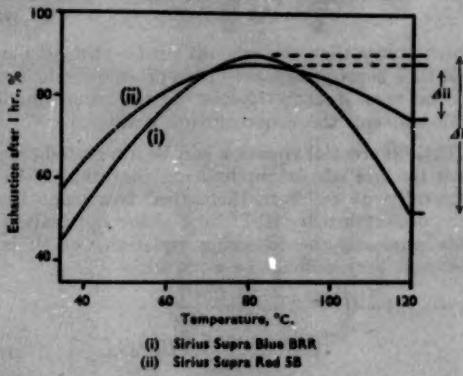
FIG. 7

The conditions are quite different at 120°c., as can be seen from Fig. 7, which shows the different changes in the state of equilibrium of the two dyes between 85° and 120°c. If, for example, we enter a viscose rayon skein, which has been dyed at 85°c., into a bath at 120°c., the equilibrium concentration corresponding to 120°c. is at once established at the surface of the fibre, while the concentration in the interior of the fibre is still the equilibrium value corresponding to 85°c. The greater this difference, the more rapidly will desorption take place. From Fig. 7 we can see that this difference is considerably greater with Sirius Supra Blue BRR (Δi) than it is with Sirius Supra Red 5B (Δii) and that the former dye is desorbed much more rapidly than the latter.

These differences do not disappear at the second stage— absorption by the undyed fibre— since the more rapidly desorbing dye produces a higher concentration in the dyebath and this leads to quicker reabsorption by the undyed fibre.

In this way an at first sight unexpected fact, that the levelling power of different dyes changes in a different manner with rising temperature, can easily be explained by careful consideration of the

separate processes into which the phenomenon of levelling can be analysed. The fact that, generally speaking, better levelling power is observed at elevated temperatures is of course connected with the decrease in swelling of the fibre already mentioned, since this considerably facilitates circulation of the liquor within the goods.

2. VAT DYES

The laws which have been derived for direct dyes are also applicable in principle to vat dyes [11]. Only the orders of magnitude are different, in some cases very different. The method of treatment is very similar to that previously adopted. And yet we shall reach other conclusions.

The stability of the majority of vat dyes in high-temperature (120°C.) dyeing is very poor [12, 13]. For example, this applies to the group of blue dyes derived from indanthrone, since, as is well known, they show a strong tendency towards over-reduction, as is also the case with various other dyes. With all halogenated dyes there is the risk that the halogen will be either wholly or partly split off by the action of the overheated alkali. For the same reason the acylaminoanthraquinones undergo more or less rapid saponification. There are only about a dozen dyes which are sufficiently stable to withstand normal dyeing at 120°C. However, it is hardly possible to undertake vat dyeing in practice upon such a restricted basis.

The question arises whether it is really necessary in most cases to employ temperatures over 100°c. for the dyeing of vat dyes. It is well known that the difficulties in vat dyeing are mainly attributable to the "strike", i.e. the sudden and usually uneven absorption of dye. As we saw from the preceding section, however, the speed of absorption depends mainly— apart from the diffusion coefficient, which also varies with temperature— upon the equilibrium concentration (cf. equation (vii)).

(i) Sirius Supra Blue BRR
(ii) IW vat dye
(iii) IK vat dye
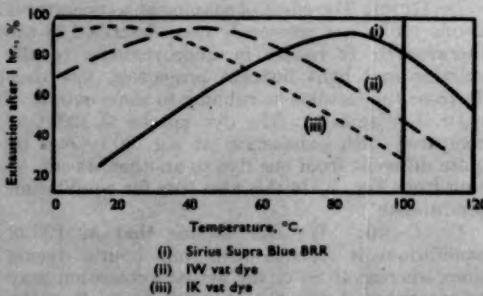
FIG. 8

It is extremely informative to compare the affinity of vat dyes with that of direct dyes, since both classes of dye follow in principle roughly the same laws. Comparison of Sirius Supra Blue BRR with an IK dye and an IW dye (Fig. 8) shows that, with a vat dye, a decrease in equilibrium concentration on the fibre is reached at 90°c. which requires a temperature of 120°c. with a direct dye.

The practice of carrying out vat dyeing at 90°C. and 100°C., or at least starting at these temperatures, has been known for many years and has been increasingly adopted of late. If very pale and delicate colours are required, dyeing is done to pattern at this high temperature. Any loss in dye caused by the low substantivity is of little importance. With deeper colours, however, it is usually advisable to dye whilst the temperature is falling, so that maximum exhaustion of the dyebath takes place. A certain amount of experience in this method is necessary, since this exhaustion has to be taken into account when matching.

The finely dispersed brands of dyes, recently developed by various dyemakers, make it possible to obtain satisfactory initial pigmentation of the package, so that in many instances there are sufficient opportunities for obtaining satisfactory results by the above method.

It is not disputed that for certain purposes, such as the dyeing of cakes and cheeses or the application of a markedly IN dye, further reduction in the affinity by raising the temperature to 120°c. can be of advantage. However, in such cases it is advisable to use special methods, such as those described by L. Drijvers and M. R. Fox.

L. Drijvers [14] gets round the risk of dye decomposition by means of his so called "integration dyeing method". The unvatted dye is added very slowly to the dyebath with the aid of a special device in the Steverlynck dyeing apparatus. This prevents the vat dye from being subjected to decomposing influences for too long whilst in a dissolved and non-absorbed state.

M. R. Fox [12] describes another method. He suggests keeping the high-temperature period as short as possible, viz. 5–15 min., so that the strike is avoided but on the other hand no perceptible decomposition of the dye takes place. Dyeing is then completed at a lower temperature, in a similar manner to that previously described for direct dyes.

3. THE SYNTHETIC FIBRES

In the course of this paper we have attempted to assess the results of practical experience, and to explain and give them coherence by applying simple, approximate formulae. We have paid special attention to the high-temperature dyeing of regenerated cellulose, since very complete numerical data are available in this field. However, the dyeing of the many different synthetic fibres at temperatures above 100°c. is of still greater practical importance.

The theoretical principles and even the mathematical formulae used also apply to the dyeing of these fibres. It is immaterial whether we explain the dyeing mechanism by absorption of dye on the micellar walls or by solubility in the substrate. The energetic and kinetic treatment of the problem leads to the same laws. It will, of course, be

readily understood that the often completely different physical properties of the fibres and the variation in their fine structure produce differences in the values for affinity and diffusion constant, and particularly in their dependence upon temperature. However, knowledge of the relationships will also assist here in filling in the gaps in this still incompletely explored field.

COLORISTISCHE ABTEILUNG

FARBENFABRIKEN BAYER AG.

LEVERKUSEN-BAYERWERK

GERMANY

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Discussion

Mr. A. S. FERN: Fig. 4 is difficult to understand, and it is not clear whether this is derived from theoretical considerations or experimentally. If the latter, it would be interesting to know the exact experimental conditions employed. It follows from Fig. 4 that there is some temperature between 50° and 85°C. (approx. 60°C.) at which the initial rate of dyeing (as measured by the slope of the exhaustion–time curve) is the same as that at 120°C. Which dye shows this behaviour, and under what conditions?

Dr. F. GUND: The graphs in Fig. 4 were determined experimentally under the following conditions— 2% dye, 10% sodium sulphate, liquor ratio 20 : 1. The exhaustion was estimated at short intervals. In the case of the dyeing at 120°C., the dyed material was removed from the dyebath at the actual temperature by means of an electromagnetic device before the pressure was released to open the autoclave.

Mr. H. R. HADFIELD: I take it that in Fig. 4, if the amount of dye absorbed were expressed as c_t/c_∞, the normal picture would result—i.e. dyeing rate increases as the temperature is raised.

The effect of the initial amount of dye absorbed being the same at two widely different temperatures can be explained as follows. The amount of dye absorbed depends upon the diffusion coefficient and the diffusion gradient. As the temperature is increased, the initial concentration gradient is decreased, but the diffusion coefficient is increased. At two temperatures these two opposite effects can compensate for each other.

Dr. GUND: I agree entirely with Mr. Hadfield's manner of considering this problem, which helps to answer Mr. Fern's question.

Mr. H. W. PARTRIDGE: What concentrations of oxidising agents (Monochrome Mordant and potassium chlorate) are recommended to prevent reduction of dye at 120°C.?

Dr. GUND: In the majority of cases the quantity of sodium chromate in the dyebath was 0·125–0·25 g./litre. The largest amount used was 0·5 g./litre.

Mr. PARTRIDGE: Is there any danger that the use of oxidising agents in the dyebath at 120°C. may cause degradation of the cellulose?

Dr. GUND: The influence of oxidising agents in the dyebath upon the fibre was examined, but no serious damage was found when dyeing at elevated temperatures, even when the dyeing period was extended to more than one hour.

Mr. S. BURGESS: In our experience the dyes rather than the fibres are likely to be adversely affected by such oxidising agents, and they must therefore be carefully selected for this purpose. Could the author supply up-to-date lists of dyes which could be dyed successfully by the method suggested?

Dr. GUND: In the experiments described in the paper sodium chromate was actually used in the majority of cases. The effect of this chemical, under the conditions described in the paper, is not very pronounced, but a few dyes susceptible to chromium as a complex-forming metal undergo a certain change of colour. Lists of suitable dyes have been given by Herrmann [1,2].

Dr. M. BRAEUER: Has aftertreatment of dyeings, e.g. vat dyeings on cotton, at high temperatures (over 100°C.) been investigated, and if so with what result?

Dr. GUND: The effect of soaping at temperatures above 100°C. has previously been described in the literature [15]. It results in improvements to the chlorine and light fastness properties, but may decrease the fastness to rubbing to some extent.

Dr. J. WEGMANN: The dye uptake at 120°C. as compared with exhaustion at e.g. 80°C. can be quite different from one dye to another, as can be seen from Fig. 7. Is this also true for equilibrium conditions?

Dr. GUND: We can assume that at 120°C. equilibrium is reached after one hour's dyeing time, whereas at 80°C. the actual exhaustion may be somewhat, but not very much, lower than the equilibrium value. These differences from one dye to another will still exist under equilibrium conditions.

Dr. WEGMANN: It would be expected from this that the difficulties of dyeing dye mixtures with falling temperature from 120°C. to 80°C. would be at least as great as when dyeing normally by gradually raising the temperature. The fact that dyes of similar exhaustion under normal conditions

show such big differences at 120°c. seems an indication that sites of different attractive power exist in the cellulose fibre which become evident at high temperatures; that is to say, sites permitting fixation of a highly substantive dye are no longer capable of retaining another dye of lower substantivity.

A certain parallelism with sites of different attractive power can be seen by comparing normal cotton with dead cotton, which under normal conditions is dyed only by highly substantive dyes.

Dr. GUND: As pointed out in the paper, difficulties regarding uneven dyeing were encountered when the dyebath was cooled down too quickly from 120°c. This applies also to mixture dyeings, and the danger of uneven dyeing during this step is, of course, greater in those cases where big differences in the exhaustion values of the dyes exist. Consequently, the method recommended in the paper, viz. allowing a longer period nearer 100°c. following a short period of dyeing above 100°c., is advisable.

The effect of high-temperature dyeing on dead cotton, as compared with normal cotton, has not yet been studied in our laboratories.

Dr. WEGMANN: Is anything known about a parallelism between the substantivity of a dye and the resulting percentage exhaustion at high temperatures?

Dr. GUND: At the moment no comparative evaluation of dye substantivity as compared with decrease of exhaustion at temperatures above 100°c. is available.

Dr. N. LANDQVIST: Attention may be drawn to the changes in the internal structure of rayon which can be produced by pressure steaming. Since X-ray analysis gives results which may indicate a change in size and shape of the crystallites, and the dyeing properties also change at the same time, such a treatment may produce suitable "model" fibres. The modifications introduced can be controlled, and a number of "unknown" factors connected with the use of cotton can be avoided.

Mr. J. PORTER: Can the author give any idea of the percentage extra cost of bulk dyeings of direct dyes (medium depth) carried out (a) by the high-temperature method and (b) by the normal dyeing method?

Dr. GUND: At the moment no cost comparison between the two processes is available. Obviously, in the high-temperature dyeing method there will be extra expenditure on machinery and additional heating costs, but these are compensated to some extent by savings in labour, as the dyeing time is reduced.

Mr. H. À BRASSARD*: It has been known for many years that some direct dyes are severely attacked by prolonged heating even below the boil. Is the blue range particularly sensitive, and if that indeed is so, why?

The protective agents used before the war were, in fact, quite simple inorganic products, and Dr. C. M. Whittaker published the one he recommended, although I think that the chemical advocated by the former I.G. was the better of the two.

I do think that it is often forgotten that instructions for dyeing this or that dye are often given with recommendations of treatment "at the boil". What a loose term this is, as no liquor in an open machine will ever reach the boil, and in dyehouses a liquor temperature in a jig, a winch, or a box will rarely be above 85–90°c. May I draw the attention of all dyemakers to this point?

Dr. GUND*: Among the blue direct dyes are quite a number of long-chain trisazo dyes which contain azo groups linked in the 1:4 position to phenylene or naphthylene residues. Dyes of this type are found to be more or less sensitive to prolonged heating in the dye liquor.

* Communicated

Review of the Symposium

Mr. D. A. DERRETT-SMITH (*Chairman of the Symposium Committee*) said that he wished to make a few observations with the object of helping to crystallise members' immediate impressions of the Symposium. The thirteen papers had indicated that the Committee could claim a fair measure of success for its endeavours to provide papers with a practical bias and without too much theory.

There had been one very practical paper on kier boiling, presented in a most stimulating way, with its strong appeal for the application of the fluidity test as a method of works control. The fundamental difference between the solubility number and the fluidity value had already been explained by Dr. T. E. Ellison*. The former test had already been instrumental in raising the standard of linen bleaching in Northern Ireland, and in the future the more sensitive fluidity test would raise it still higher.

Three papers had been concerned with bleaching. None had been devoted entirely to Northern Ireland's main textile product— linen— but it had been referred to in the paper by Crowder and White and had been considered in the course of the discussions.

The six papers devoted to dyeing had been of great practical value, since they had been concerned with such up-to-the-minute topics as continuous dyeing, high-temperature dyeing, and the dyeing of Tricel and Terylene, including the first account in English of the new Swedish Pad–Roll system of dyeing.

Of the two papers dealing with the resin finishing of textiles, the first had described an academic investigation of the conditions of application of urea–formaldehyde precondensates and their subsequent baking, the results of which, if confirmed, might well lead to fundamental changes in design of plant. The second paper had the thoroughly practical aim of the prediction of resistance to wear, and again the results might well be of wide significance. Both papers aimed to make it easier to get the right result than the wrong one, which is what we should all aim at.

The third paper on finishing described an attempt at a scientific investigation of raising, a difficult process to study systematically, but one which was rapidly coming back into fashion.

Finally, Mr Derrett-Smith said that he had found all the papers not only to supply some material facts but also to stimulate his own ideas. If all those attending had received equal benefit, the Symposium would have been successful in achieving what it had set out to do.

Mr. FRED SMITH (*President of the Society*) formally closed the Symposium by thanking, on behalf of the Society, all who had worked so hard to make the Symposium an outstanding success.